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IMPROVEMENT OF INSTRUMENTATION AND METHODOLOGY FOR COLLECTION AND ANALYSIS OF MERCURY

D. J. Sibbett, et al

Geomet, Incorporated

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January 1975

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IMPROVEMENT OF INSTRUMENTATION AND METHODOLOGY FOR COLLECTION AND ANALYSIS OF MERCURY

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16. ABSTRACT

A collection device for the sampling of atmospheric mercury in its three forms, previously developed under EPA contract 68-02-0578, was miniaturized and streamlined and methods for the recovery and analysis of the collected mercury were simplified.

The device consists of a two-section canister assembly which fits inside a standard Hi-Vol sampler underneath the support screen for the particulate filter. While particulate mercury is collected in the usual manner on glass fiber filter, mercury vapors are trapped on specific absorbants, i.e. elemental mercury on silver-impregnated alumina in the upper canister section and combined mercury vapors on charcoal in the lower section. With the Hi-Vol operating at 24 CFM, an airflow of 8 - 9.5 lpm was obtained through the canister.

Recoveries averaged 101% for particulate mercury, 104% for elemental mercury and 96.3% for organic mercury compounds. Gaseous pollutants such as SO_2, NO_2 or H_2S did not affect the collection efficiency.

Procedures have been developed and tested for the recovery and analysis of elemental mercury, dimethyl mercury and mercury-bearing particulates. These methods utilize standard laboratory instrumentation including an induction combustion furnace and an atomic absorption spectrophotometer. The precision of the methods is indicated by the standard deviation of the results which is in the $\pm$ 6-8% range.

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by

D. J. Sibbett, R. H. Moyer and T. R. Quinn

Geomet Incorporated
2814 A Metropolitan Place
Pomona, California 91767

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EPA Project Officer: Eva Wittgenstein

Chemistry and Physics Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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January 1975

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Section 1.0

BACKGROUND AND OBJECTIVES

This contract was a continuation of effort originated under EPA Contract No. 68-02-0578 for the development of a collector for all forms of atmospheric mercury which operated in conjunction with a conventional High-Volume particle sampler. In this procedure, mercury is collected in particulate and vapor forms. The latter is further separated into elemental mercury and all other mercury compound vapors.

The technical objectives of the current program included (1) miniaturization of the vapor sampling techniques which utilized absorbents, so that the High-Volume sampler package might be operated without the addition of complex or bulky modifications and, (2) simplification of the techniques for recovery and analysis of the three forms of mercury in ambient air. Commercially available instrumentation is required in analysis and quantitation of mercury-containing samples. The latter are extracted from ambient air over a range extending from a few nanograms per cubic meter to 100 micrograms per cubic meter. To verify achievement of these objectives, full descriptions of (1) the modified collector, (2) experimental operating and analytical procedures and (3) supportive test data are required. Section 3.1 details the miniaturization, Section 3.2 describes the experimental techniques which were applied in testing and sample analysis and Section 3.3 contains the data which were collected to establish the utility of the methods.

Section 2.0

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

2.1 SUMMARY

The technique of collecting vaporized forms of mercury by utilization of absorber canisters in conjunction with a High-Volume sampler which collects mercury-bearing particulates has been miniaturized to fit the entire added assembly within the normal configuration of such instruments. As adapted, vapors from elemental mercury and organo-mercury compounds are collected by passage of air through a canister containing two selective absorbents which is positioned within the collector funnel of a High-Volume sampler. A fully assembled cylindrical collection canister measures 11.74 cm (high) x 3.18 cm (diameter) including its screen-containing end pieces. It may be conveniently transported by mail to laboratories for analysis in standard 12.7 cm x 4.45 cm mailing tubes.

Each sampling canister consists of two cylindrical sections, 2.54 cm (i.d.) x 5.08 cm (high), fabricated from polyvinyl chloride (VT-36) plastic tubes which are joined together by a screen holder and closed off at each end by another screen holder. Canister sections are filled separately by absorbents which are selective for vapors of elemental mercury and combined mercury, respectively.

Canisters are supported within the High-Volume sampler assembly by a large orifice plate which has six, 0.64 cm (diameter) holes spaced equally on a 7.14 cm radius. In normal operations at an air sampling rate of 24 CFM, two of these air flow orifices are closed off. The orifice plate supports a canister orifice housing, a retaining

ring, a canister flow orifice, differential pressure taps and a canister clamp. Air flow through the central canister portion of the sampler is controlled by the canister flow orifice; the flow rate is measured, after calibration, by placing a differential pressure meter across this orifice. The canister support assembly is fixed in position when the knurled ring which attaches the High-Volume sampler funnel to the blower housing is tightened.

With a conventional glass fiber filter positioned on top of the sampler funnel and a canister placed in the added assembly, the High - Volume sampler may be used to sample air for mercury particulates, elemental mercury and vapors of mercury compounds.

Three absorbents were tested in a laboratory apparatus for suitability for collection of elemental mercury: (1) silver wool, (2) 10% silver on alumina support and (3) a silver zeolite. Silver wool collected efficiently at air flows of approximately 200 ml/min. The granular materials collected effectively to rates of approximately 10 liters/min. However full recovery of mercury from the silver zeolite was not achieved. Therefore, the absorbent consisting of 10% silver on alumina was selected for testing.

Collection efficiency tests were run with the High-Volume sampler operating at 24 CFM and the canister sampler at 8.0-9.8 liters/min. Five different types of tests were conducted including collection and analysis of: (1) elemental mercury, alone, (2) dimethyl mercury, alone (3) mercury-bearing (HgS) particulates diluted in silica, (4) elemental mercury and dimethyl mercury together in the presence of hydrogen sulfide, sulfur dioxide and nitrogen dioxide and (5) ambient air samples.

Elemental mercury was sampled in the concentration range from 0.044 to 201 $\mu g/m^3$ with the canister operating at 9.8 liters/minute. In tests, recovery averaged 104%; the standard deviation of the results was 18.8%.

Collection of mercury organics utilized dimethyl mercury as the test compound. Laboratory efficiency tests were conducted at levels from 0.57 to 113.2 $\mu g/m^3$. Recovery of dimethyl mercury averaged 96.3% in ten tests; the standard deviation of these results was $\pm$ 11.5%.

Collection of particulate mercuric sulfide diluted in fumed silica (Cab-O-Sil) was conducted with a total particle loading on the glass fiber filter varying between 2610 and 19200 μg. This range was equivalent to 384.2 to 471.1 $\mu g/m^3$. In eleven tests, recovery averaged 101% with a standard deviation of $\pm$ 5.1%.

Tests of collection and analysis of both gas phase components were carried out in the presence of added gases which might potentially interfere with the performance of the collector canister. Hydrogen sulfide (1.2 ppm), sulfur dioxide (5.0 ppm) and nitrogen dioxide (3.2 ppm) were added in tests of collection of elemental mercury and dimethyl mercury. Essentially, the collection and recovery characteristics were not changed by the added gases. Total recovery of elemental and dimethyl mercury averaged 99.4% ($\sigma = \pm$ 6.3%) in 28 tests. Elemental mercury recovery was 99.9% ($\sigma = \pm$ 7.0%); dimethyl mercury recovery was 98.2 ($\sigma = \pm$ 7.9%) for the same runs. These data confirm the ability of the canister collection method to operate successfully in reasonably contaminated atmospheres.

A series of 8 - 24 hours tests of the collection procedures were run in ambient atmospheres characteristic of the environment of the laboratory. In the room used for storage of elemental mercury and dimethyl mercury, levels of 0.023 - 0.028 $\mu g/m^3$ of elemental mercury and 0.015 to 0.026 $\mu g/m^3$ of dimethyl mercury were detected. In the shop area levels from 0.025 to 0.049 $\mu g/m^3$ of elemental mercury were obtained. Organic mercury was not detected. At the building entrance, levels from 0.010 to 0.024 $\mu g/m^3$ in elemental mercury were measured. Although measurable deposits of particles were obtained in all locations, mercury bearing particulates were very low varying from 7×10^{-5} to 1.2×10^{-3} $\mu g/m^3$.

The environmental factors, temperature and relative humidity were measured for the major portion of the test data. No effects on collection or analysis were observable.

In order to test for factors of the total procedure relating to handling, storage and shipping, a set of canisters (a blank and a controlled sample) were shipped by mail from the west coast to the EPA Research Triangle Center, opened, inspected and returned. On return, the silver-alumina and charcoal absorbents were reanalyzed. No significant change in mercury content of either material was detectable. Thus, this simple procedure of sample transmission by mail appears adequate to send field samples to a central analytical laboratory.

Procedures have been developed and tested for the analysis of elemental mercury absorbed on silver-alumina, dimethyl mercury on charcoal and mercury-bearing particulates on the standard 8 x 10 inch

glass fiber filter used by High-Volume air samplers. The precision of these analytical methods is indicated by the standard deviation of the results, which is in the $\pm$ 6-8% range, normally. The methods developed utilize standard laboratory instrumentation including an atomic absorption spectrophotometer and an induction combustion furnace.

2.2 CONCLUSIONS

A prototype field procedure for collecting particulate mercury and the vapors of elemental mercury and organic mercury compounds from air samples by utilization of a standard High-Volume air sampler has been developed and tested. Samples collected by the technique may be shipped in simple mailing tubes to a central laboratory for analysis. Analytical procedures for laboratory analysis have also been developed and tested. Initial testing of all aspects of the method is complete. The methods applied appear to form a sound basis for batch sampling of mercury under a variety of field conditions.

2.3 RECOMMENDATIONS

Testing of the collector method under a variety of conditions should be conducted to establish acceptance of the methods which have been developed. The limits of the field uses which may be appropriate have not been determined. However, the techniques and methods which have been developed have no obvious limitations.

In short, the recommendation arising from this work, is, that the technique be used wherever mercury evaluations are required. The method is not appropriate for real-time or nearly real-time determinations.

Section 3.0

DETAILED TECHNICAL REPORT

3.1 MINIATURIZATION OF THE COLLECTION DEVICE

The collection device previously developed under Contract No. 68-02-0578 has been redesigned so that collection of the various forms of vapor which contain mercury is achieved by a miniaturized canister array positioned within a standard Hi-Vol sampler. Particulate collection remains, as previously demonstrated on the standard glass fiber filter of the Hi-Vol sampler.

Schematically, the arrangement utilized is shown in Figure 3-1. The mercury vapor sampling assembly has been installed within the funnel of a Hi-Vol sampler so that no external modifications of the sampler are required. The components which are added within the shell of the sampler are shown in more detail in Figure 3-2. The components are identified by part numbers which refer to Figures 3-3 through 3-10. These figures show all the details necessary to fabricate the canister and its support sections.

In routine operation, the two component, plastic absorption canister sits in an aluminum socket provided in an orifice housing. The assembly has two sets of orifices: one under the canister housing to control the flow of air through a canister, a second, comprising a series of six 0.64 cm (1/4 inch) holes in the plate which supports the orifice housing. These latter orifices control the total air flow through the Hi-Vol sampler. To achieve desired air flow rates through the Hi-Vol funnel and the canisters, the 0.64 cm holes were blocked as required. With two holes blocked, a 24 CFM air flow through the sampler was achieved, while simultaneously a 9.5 lpm air flow through the canister resulted when the orifice plate under the canister had a 0.13 cm (.052 inch) diameter opening.

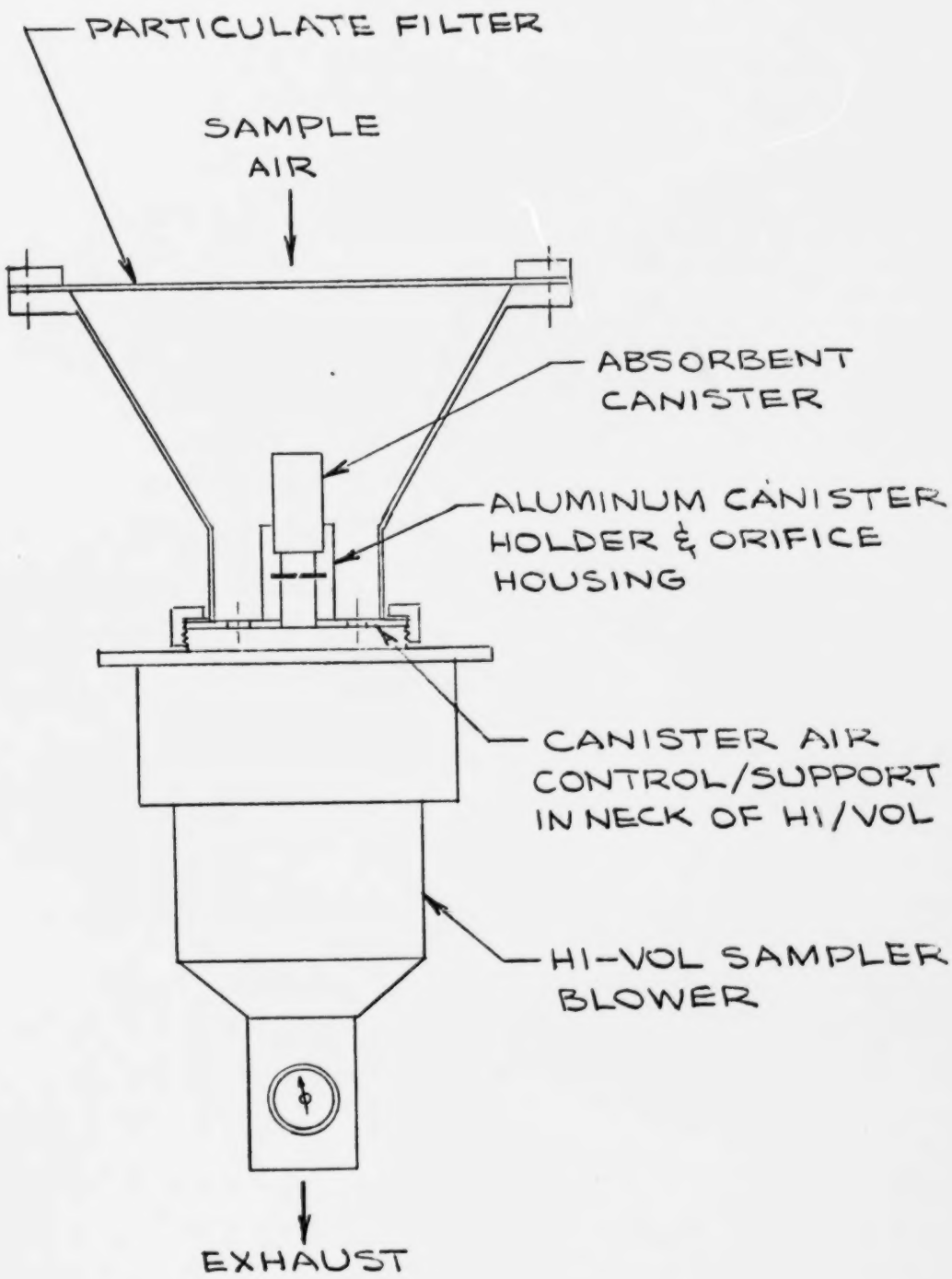


Figure 3-1
Schematic of Collection Assembly

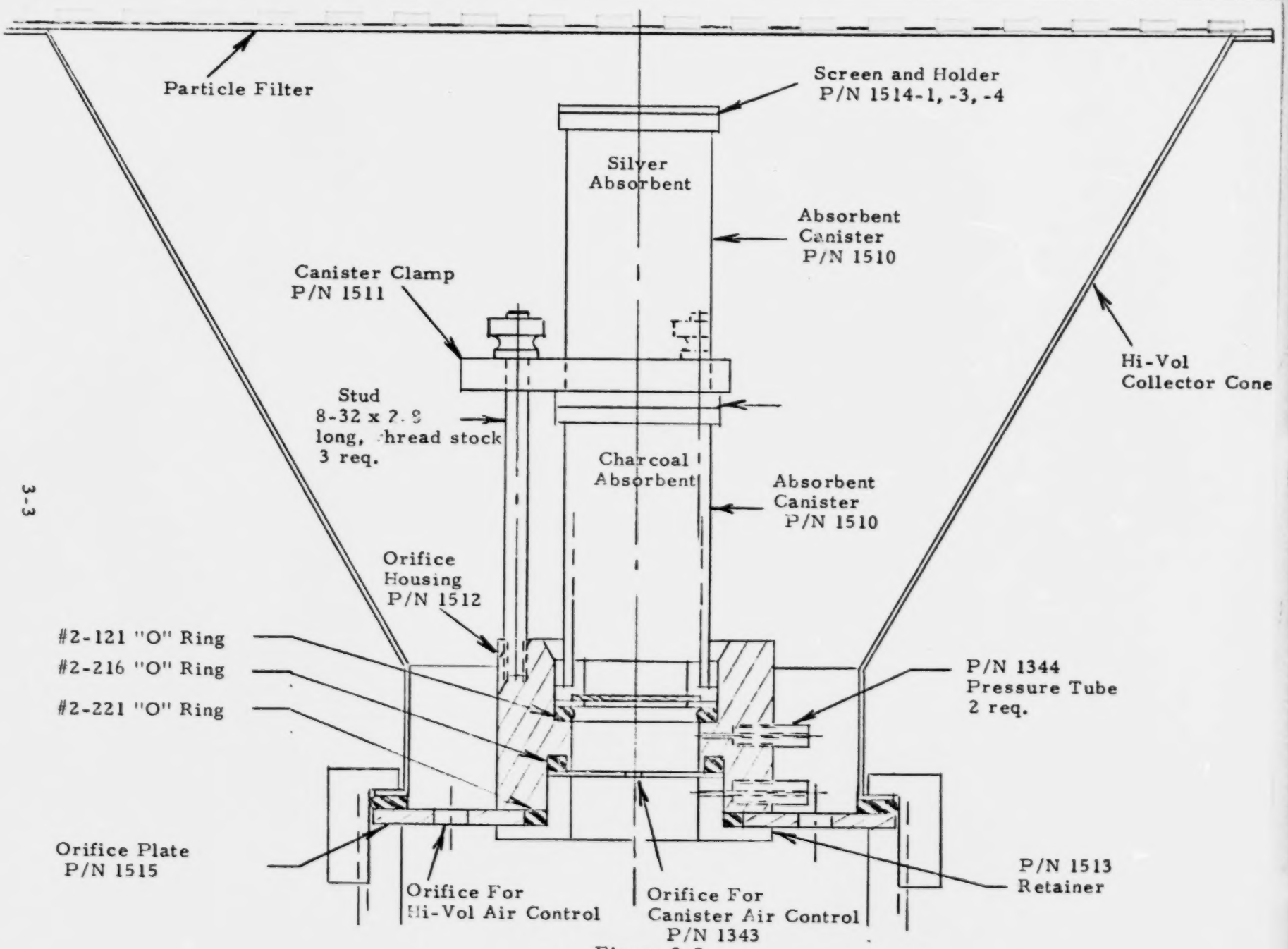


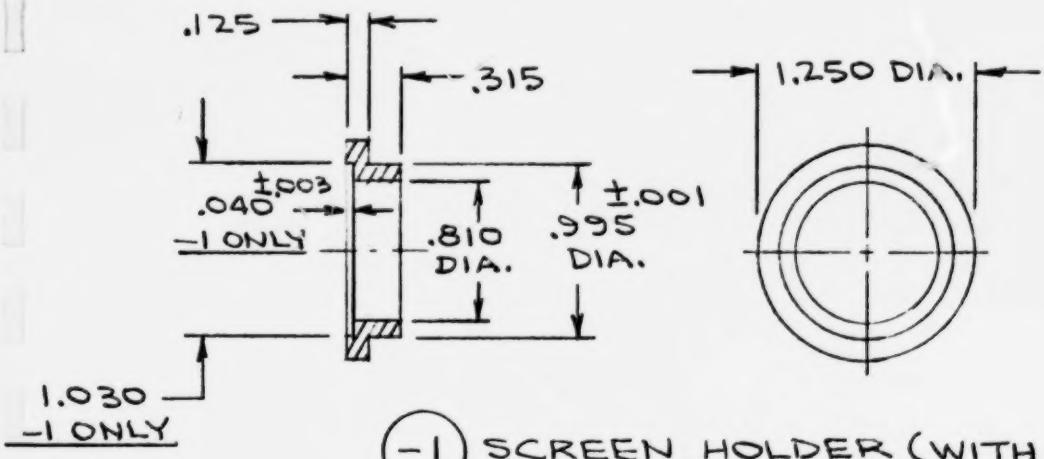
Figure 3-2

Mercury Collection in Hi-Vol Sampler

The dimensions of the canister components are shown on Figures 3-3 and 3-4. Each cylindrical section of the canister is 2.54 cm in internal diameter (0.998" i.d.) and 5.08 cm (2") in height. The volume per section is 25.6 ml. In use, these sections are each charged with 24 ml of granular absorbent.

The canisters are assembled with screens and screen retainers (Figure 3-3) separating the two absorbent sections. Screens are made of 20 mesh stainless steel and sealed into the recessed end of one of the retainers by use of Permabond No. 120 adhesive. The divider between the two sections of the canister is fabricated from 1 screen holder with recess (Figure 3-3, -1) and 1 screen holder without recess (Figure 3-3, -2). The screen is sealed to the recessed holder, then the two sections are cemented together, face to face. Finally, two canister sections as shown in Figure 3-4 are cemented to the ends of this divider and the absorbent charge is added separately to each section. On addition of each absorbent, the corresponding acrylic end pieces were sealed to the cylinder sections by use of a drop of adhesive on each side of an end screen holder. In order to make canisters easily openable for analysis, use of too much adhesive must be avoided in this last operation.

The aluminum canister holder assembly which is simultaneously a housing for the orifice controlling flow through the canister is shown in Figure 3-2. It consists of seven parts. These are (1) the Orifice Housing (Figure 3-5), (2) the Retaining Ring No. 2 (Figure 3-6), (3) the Large Orifice Plate (Figure 3-7), (4) Pressure Tubes (two) Figure 3-8), (5) the Canister Flow Control Orifice Disc (Figure 3-9), (6) the Canister Clamp (Figure 3-10) and (7) the canister bolts (three) (not shown).



(-1) SCREEN HOLDER (WITH RECESS)

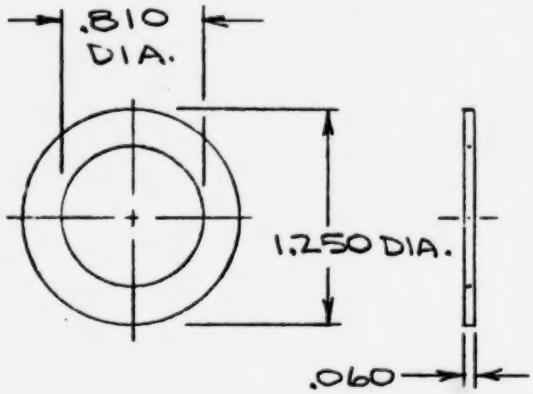
MAT.: CLEAR ACRYLIC

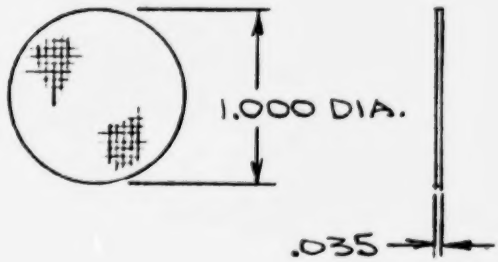
NO. REQ.:

(-2) SCREEN HOLDER (WITHOUT RECESS)

MAT.: SAME AS -1

NO. REQ.:





(-3) SCREEN RETAINER

MAT.: ACRYLIC

NO. REQ.:

(-4) SCREEN

MAT.: 20 MESH CRES

NO. REQ.:

DIMENSIONS IN INCHES

Canister End Pieces and Screens

GEOMET, INC.

Figure 3-3

1514

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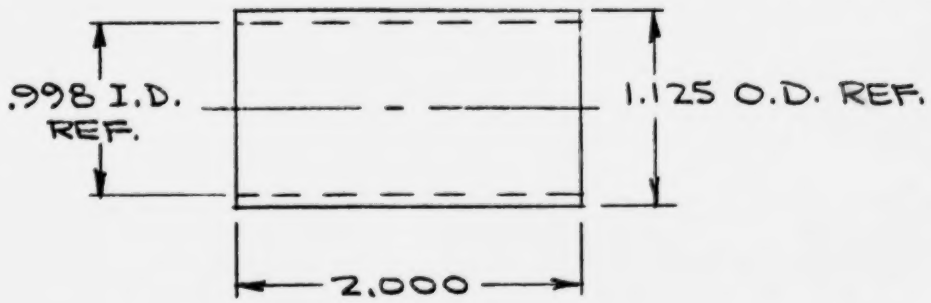
H.H.ANDERSON



CANISTER TUBE

MAT.: (EMA) VT-36 (ABS PLASTIC)

NO. REQ.:

DIMENSIONS IN INCHES

Figure 3-4

GEOMET, INC.

1510
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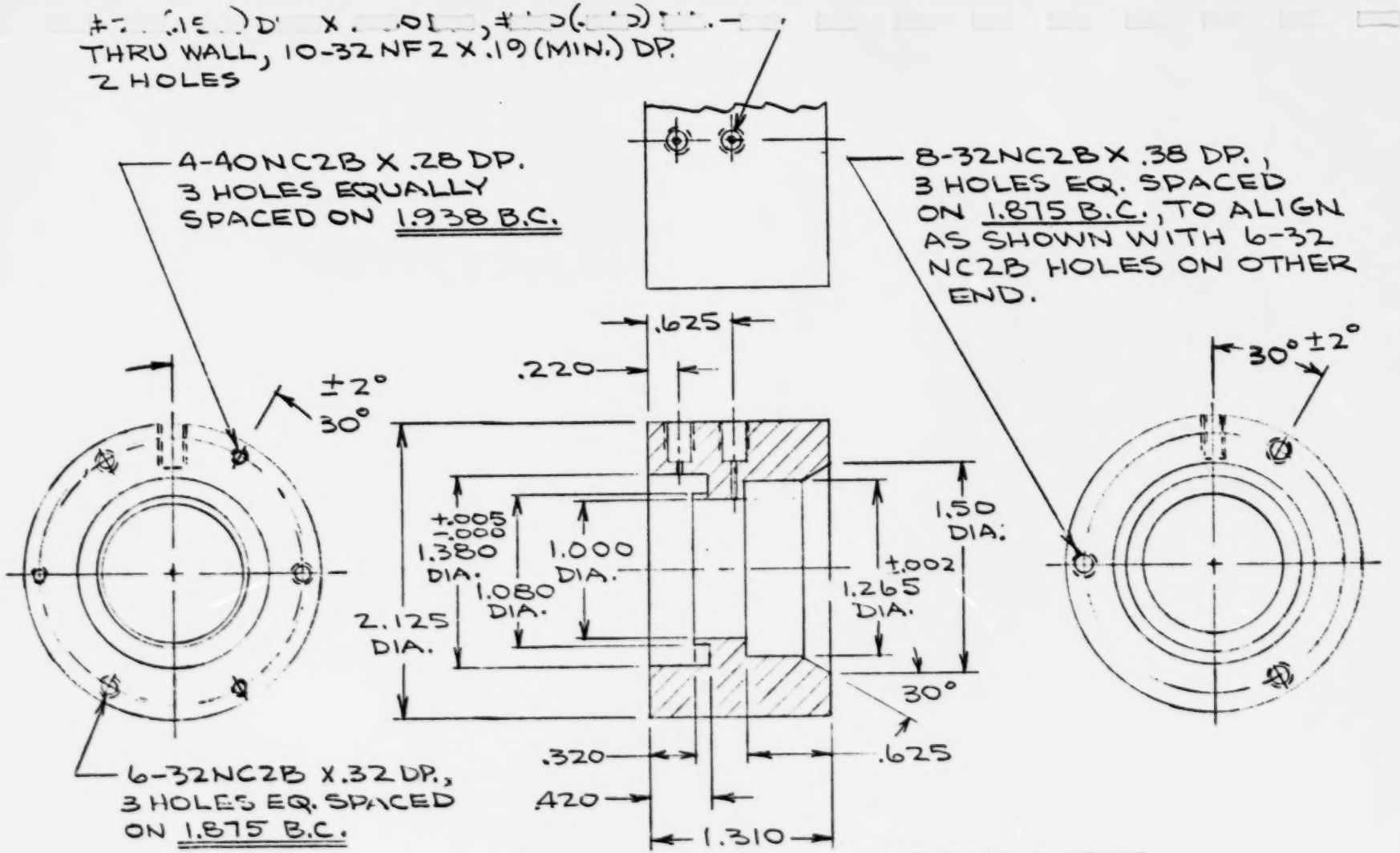


DIMENSIONS IN INCHES

ORIFICE HOUSING NO. 2

MAT.: 6061-T6 ALUM.

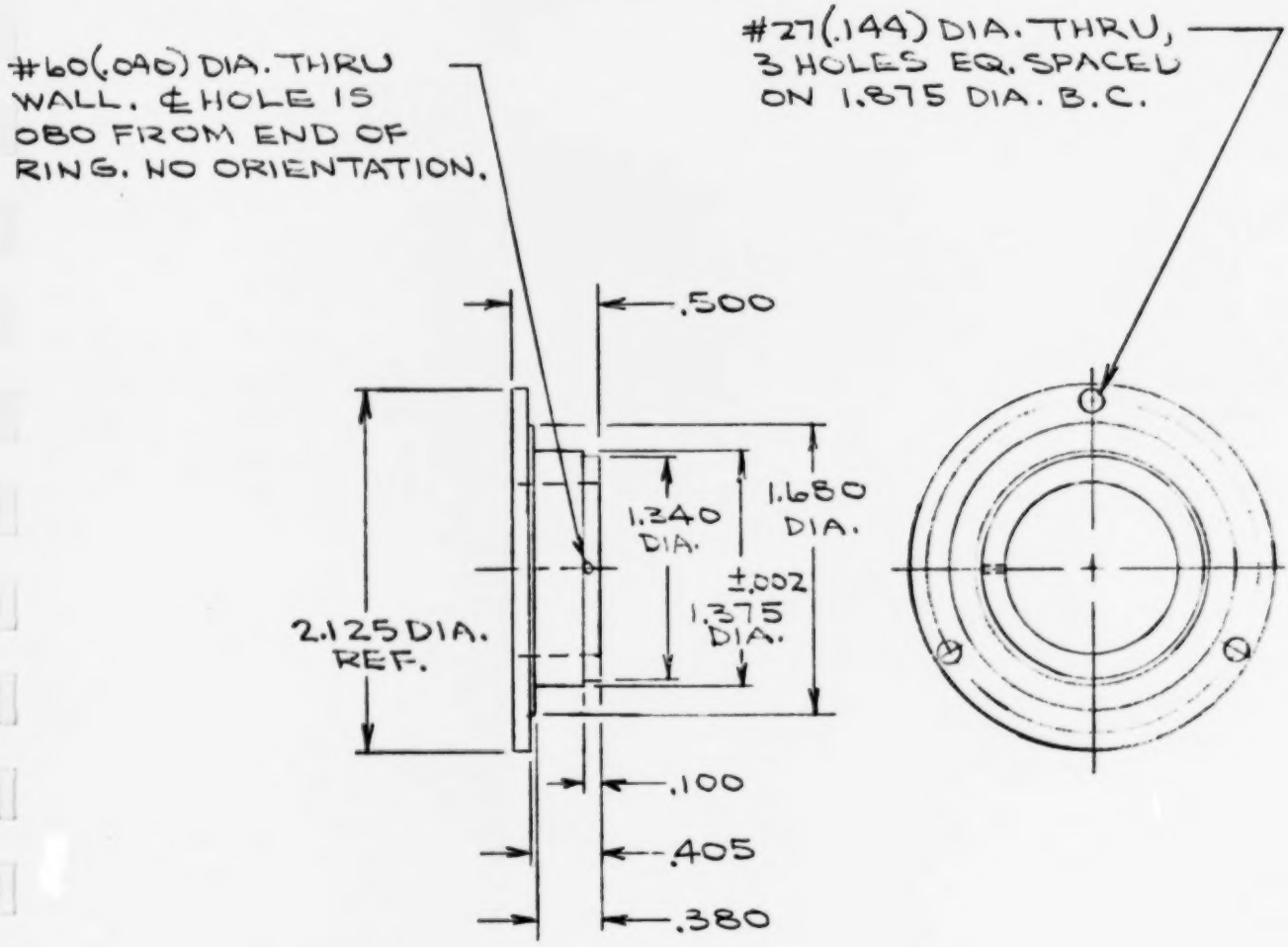
NO. REQ.:

GEOMET, INC.

1512

DRAWN BY:
H.H. ANDERSON

Figure 3-5



RETAINING RING NO. 2

MAT.: 6061-T6 ALUM.

NO. REQ.:

DIMENSIONS IN INCHES

Figure 3-6

GEOMET, INC.

1513

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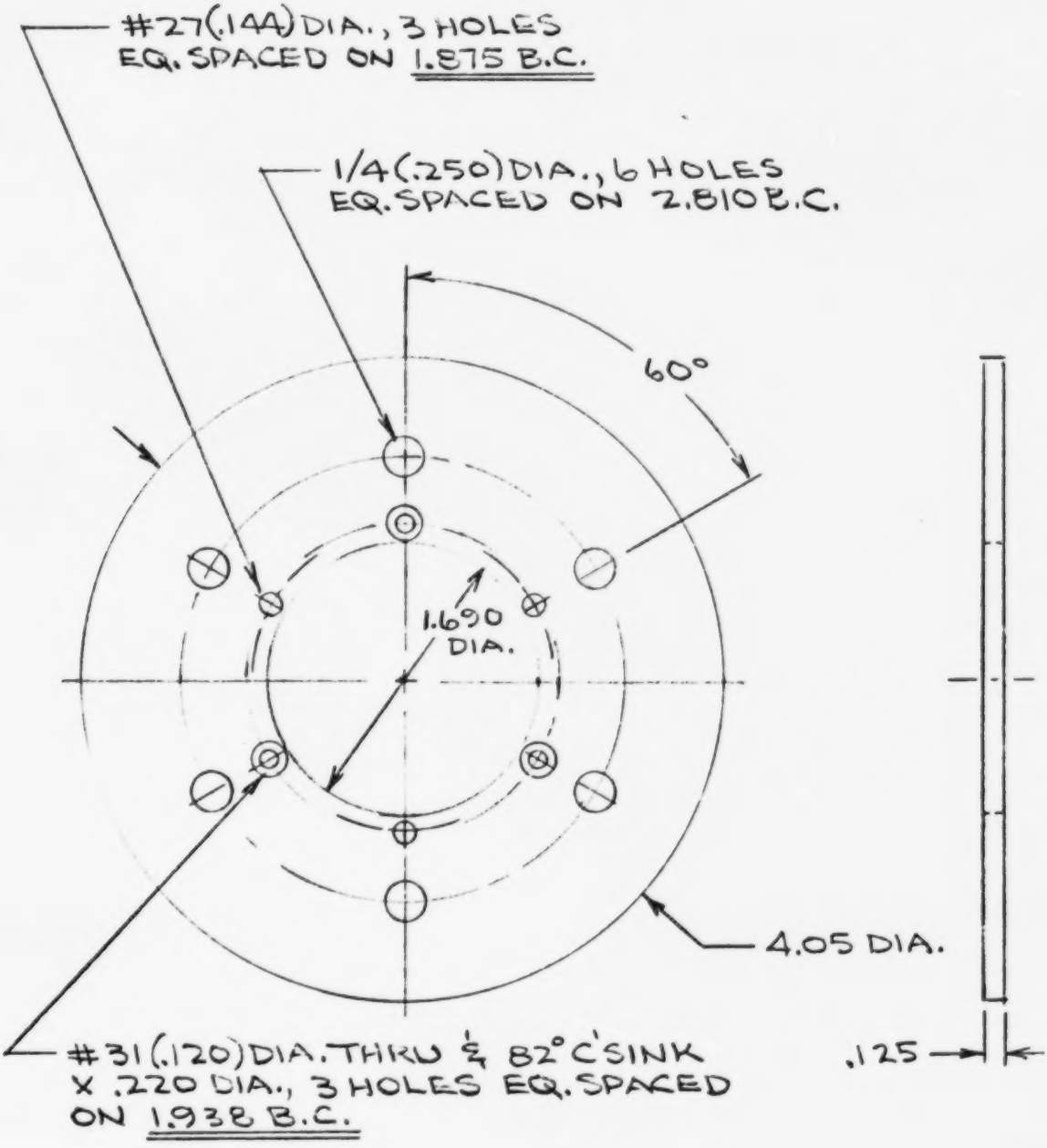

LARGE ORIFICE PLATE

MAT.: 6061-T6 ALUM.

NO. REQ.:

DIMENSIONS IN INCHES

GEOMET, INC.

Figure 3-7

1515

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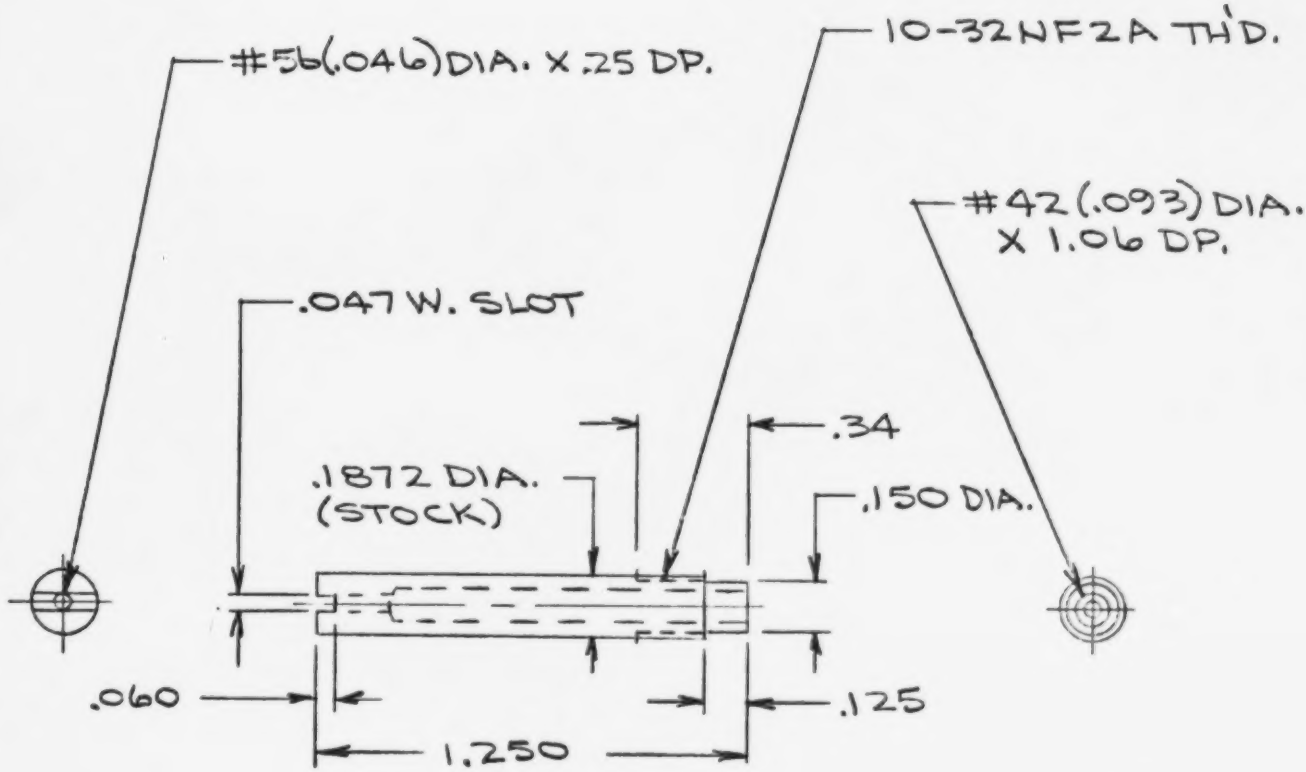

SCALE: 2 X SIZE

PRESSURE TUBE

MAT.: 303 CRES

NO. REQ.:

DIMENSIONS IN INCHES

Figure 3-8

GEOMET, INC.

1344

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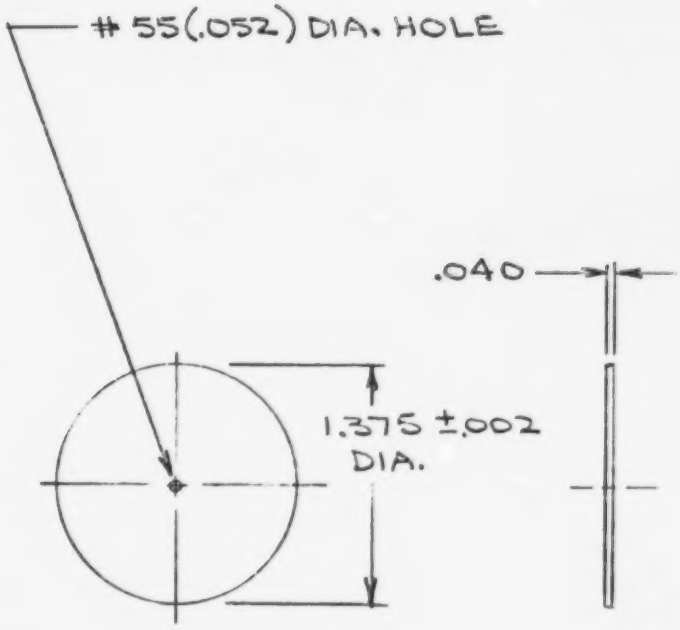
H.H.ANDERSON



NOTE: HARD ANODIZE TO .002 DEPTH

DIMENSIONS IN INCHES

ORIFICE DISC

MAT.: 6061-T6 ALUM.

NO. REQ.:

GEOMET, INC.

Figure 3-9

1343

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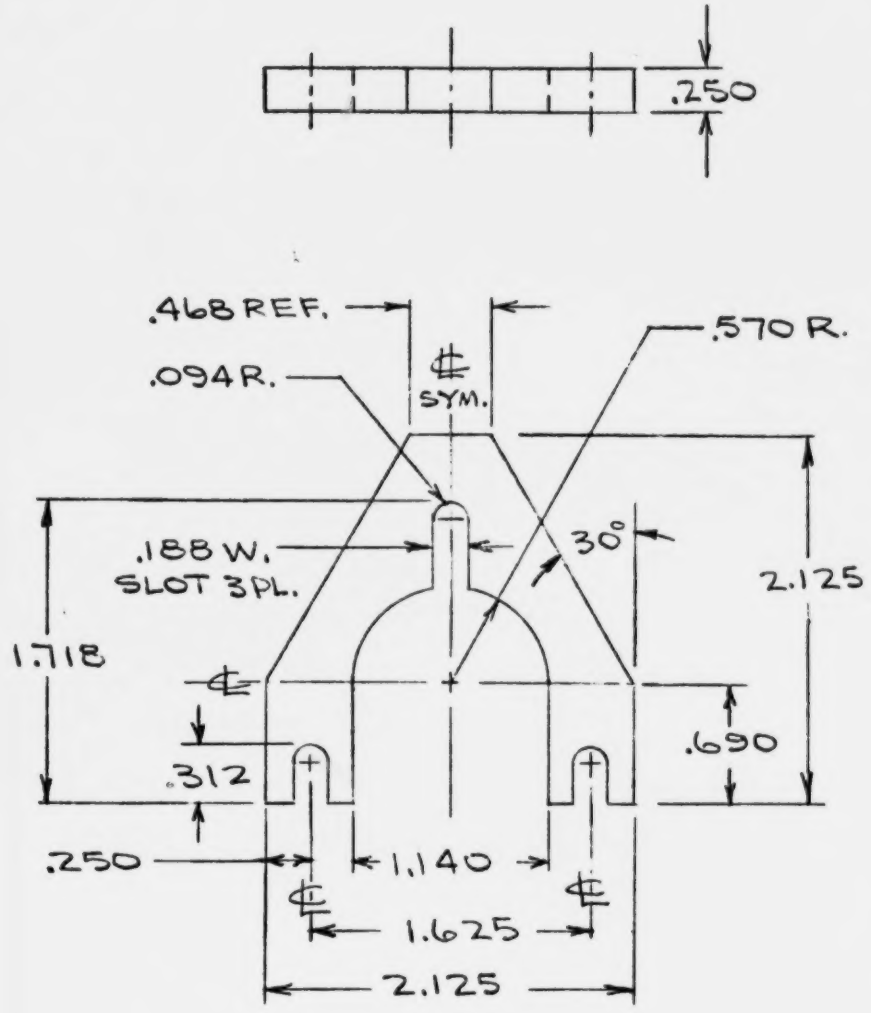

DIMENSIONS IN INCHES

CANISTER CLAMP

MAT.: 6061-T6 ALUM.

NO. REQ.:

Figure 3-10

GEOMET, INC.

1511

DRAWN BY:
H.H. ANDERSON

Differential pressure taps for calibration of air flow rates have been included. (These are capped when measurements are not required.) The canister holder bolts to the large orifice plate and the retainer. The large orifice plate functionally supports the canister holder and also controls the total air flow through the Hi-Vol sampler. The large orifice plate is placed under the flange of the Hi-Vol funnel during assembly of the sampler. Tightening of the large knurled ring then fixes both the Hi-Vol funnel and the canister sampler in position for use.

The retainer (Figure 3-6) supports the canister air control orifice plate (Figure 3-9) from the bottom side of the assembly. Canisters are fastened to the canister holder and orifice housing by three bolts and a canister clamp. The clamp fits around the middle section of the canister and is fastened on the upper side of the canister divider. The clamp is shown in Figure 3-10; the method of assembly in Figure 3-2. A canister is solidly positioned when the bolts are tightened into the orifice housing. The bolts are 0.64 cm (0.25 inch) thread stock 7.11 cm (2.8 inches) in length.

Seals at the bottom of the collection canister, between the orifice housing and the retainer and between the retainer and large orifice plate are achieved by the use of rubber "O" rings.

SUMMARY

A relatively simple two section canister collector was designed and installed in a Hi-Vol sampler without modification of the standard sampler envelope. This assembly is then applicable to the collection of mercury in all its airborne forms, particulate and vapor. Vapor collection has been separated into elemental and combined form by use of a two section canister, each section of which is specific in collection of either type of vapor. In

principle this collection technique may be employed for a variety of gaseous and particulate pollutants by modification of the absorbent species.

3.2 EXPERIMENTAL TECHNIQUES

In principle, operation of the collection system involves setting up and drawing air through the sampler, removal of the resultant samples from the collector followed by analysis of the solid absorbents and filter for mercury. All of these operations must be carried out with adequate care to achieve results of useful accuracy.

Discussions of the experimental methods employed include (1) operation of the sampler, (2) canister air flow calibration, (3) processing of elemental mercury absorbents, (4) processing combined mercury absorbents, (5) processing of mercury particulates, and (6) analysis of processed samples by the atomic absorption spectrophotometer.

3.2.1 Operation of the Sampler

3.2.1.1 Assembly of the Sampler

The miniaturized absorbent canisters described in the preceding section were prepared for use by weighing an appropriate volume of absorbent into each half. The elemental mercury absorbent was placed in the upper half into which the air passes initially. For the 10% silver on alumina absorbent which was 8-14 mesh, 24.0g were weighed into the upper section. A canister end piece was added and sealed onto the canister body with a minimum amount of Permabond No. 102. The absorbent for combined mercury vapor was added similarly to the lower end of the canister. Using Barneby-Cheney TCA Grade charcoal (6-10 mesh) 12.5 g was required to fill the lower section of the canister.

With the High-Volume Air Sampler* disassembled, assembly for use involved the following steps:

(1) Insertion of the end of the absorbent canister into the orifice housing and support assembly, followed by assembly and tightening of the retaining clamp.

(2) Placement of the large disc, canister and canister support assembly of top of the blower housing.

(3) Positioning of High-Volume Sampler funnel in position atop the blower housing. The canister and its assembly extends upward within the funnel but not as far as the level of the filter support.

(4) Tightening of the knurled ring at the funnel base onto the threads of the blower housing. This action fixes the canister and its flow controls in position.

(5) Placement of the particulate filter** on top of the stainless support screen of the air funnel and positioning of the retaining frame on the edge of the filter.

On completion of the assembly process, the pressure taps indicated in Figure 3-2 should be connected to a Magnehelic Differential Pressure Gage***. This gage may be used to measure flow through the canister after calibration. The method of calibration is indicated in the following section.

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* The High Volume Air Sampler used in the program was the Precision Scientific Model, obtained from Van Waters and Rogers Scientific, Catalog No. 10300-306.

** Standard High Volume Sampler glass fiber filters measuring 8 x 10 inches, Van Waters and Rogers Cat. No. 10300-420 were used.

*** Magnehelic Gage Model 2100C measuring 0-100 inches of water differential pressure.

Total air flow through the High-Volume Air Sampler is displayed on the gage attached into the base of the blower. With four of the six orifices in the orifice plate open, air flows of approximately 24 CFM were achieved. Under these conditions, an air flow of 8.0-9.5 lpm through the canister resulted.

3.2.1.2 Experimental

The apparatus set up to monitor introduction and collection of controlled mercury vapor samples is shown schematically in Figure 3-11. A domed section was constructed to close off the air inlet above the particulate filter of a Hi-Vol sampler. The dome was bolted to the top of the sampler using a rubber gasket to effect a seal. Air under ambient conditions was brought into the dome through a 3" (7.62 cm) i.d., side arm. Mercury vapor was brought from a controlled source into a sample inlet tube 3/8" (0.95 cm, i.d.) which extended inside the side arm. (This technique is indicated in Section 3.1.3.) Thus, mixing of the sample stream and the ambient air occurred in the side arm. The mixed sample was pulled through the apparatus by the Hi-Vol blower. By adjustment of the air control orifices in the canister support in the neck of the Hi-Vol about 1.4% of the total air flow through the sampler was diverted through the collection canister. Constancy of air flow through the canisters was checked by means of a Magnehelic gage during sampling operations. Air sampling probes (teflon) were positioned at the inlet end (Probe 1) of the canister and in the outlet (Probe 2) stream. The latter probe was positioned immediately under the charcoal-containing section but above the orifice plate under the canister. Samples at both positions were pulled into bubblers for evaluation during all runs. The mercury concentration value obtained

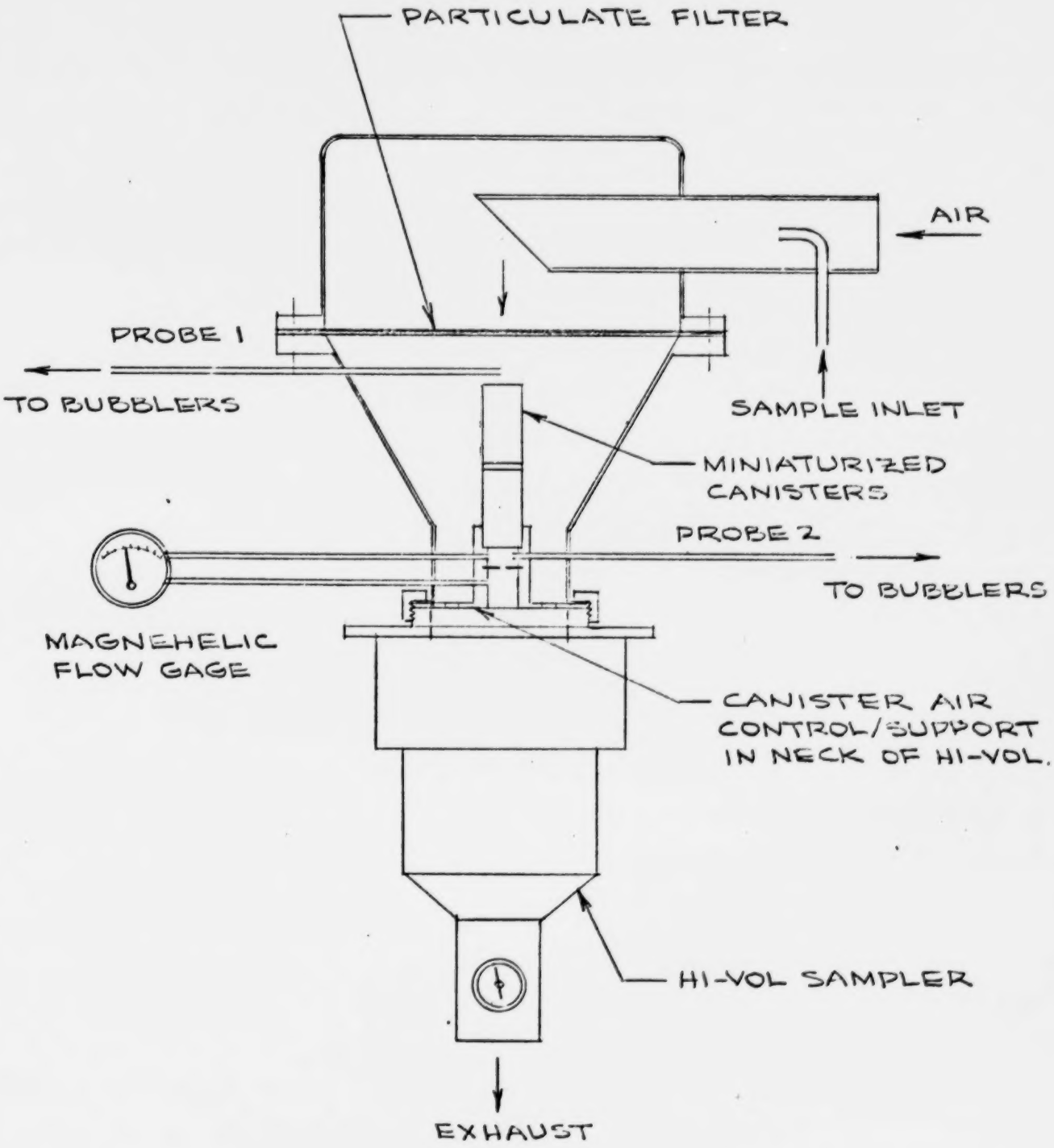


Figure 3-11

Schematic of Collection Assembly

at the upper probe was used to define the level of the source stream. The lower probe (No. 2) was used to check the efficiency of the collection.

The various air flows utilized in the sampling assembly are shown in Figure 3-12. The Hi-Vol sampler was operated at 24 CFM (~ 679 l/m). The inlet stream air which contained controlled levels of mercury vapor was added to the ambient air at 2.8 l/min. Mixing was carried out in the side arm of the inlet. A total of 9.5-9.8 l/min. of the total inlet flow was passed through the canister. At the upper end of the canister samples were taken at 1.0 l/min. into two $KMnO_4$-HNO_3 bubblers when elemental mercury alone was sampled; iodine monochloride was used for total mercury when organic mercury compounds were present. Results of analysis of the mercury trapped in these bubblers were used as the source level. At the lower end of the canister another gas sample to two bubblers was taken at a flow of 1.5 l/min. Analytical results from this position were used to define the performance efficiency of the canisters.

Air flow was measured as follows: (1) the total sampler flow was monitored from the air flow gage placed below the instrument blower*. (2) The inlet and outlet bubbler flows were measured with rotameters which were placed between the second bubbler in each set and the vacuum pumps (Neptune Dyna Pumps, either Model 2 of Model 4K) used to draw the air. Flow was adjusted by valves placed between the rotameters and the pumps. (3) Air flow from the mercury source was measured by rotameter placed on the outlet side of a Dyna Pump which was used to push air through the mercury source. Figure 3-13 shows this arrangement. From the rotameter, air passed over a pool of mercury held in a U tube and thence directly to the sample inlet in the side arm of the dome over the Hi-Vol.

* The Hi-Vol is a Precision Scientific Model, Cat. No. 63083. This gage réads directly in CFM.

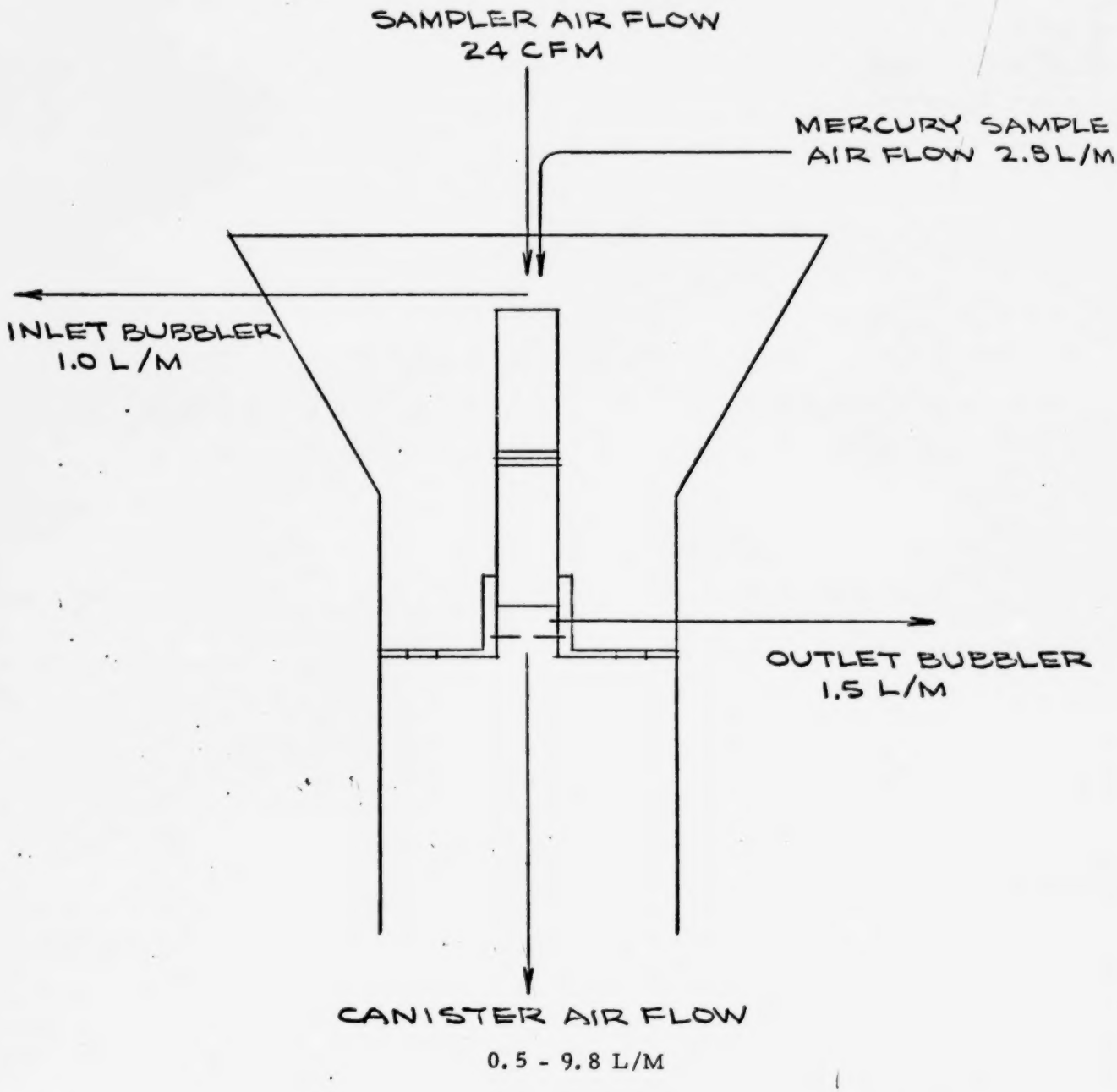


Figure 3-12

Air Flows in Sampling System

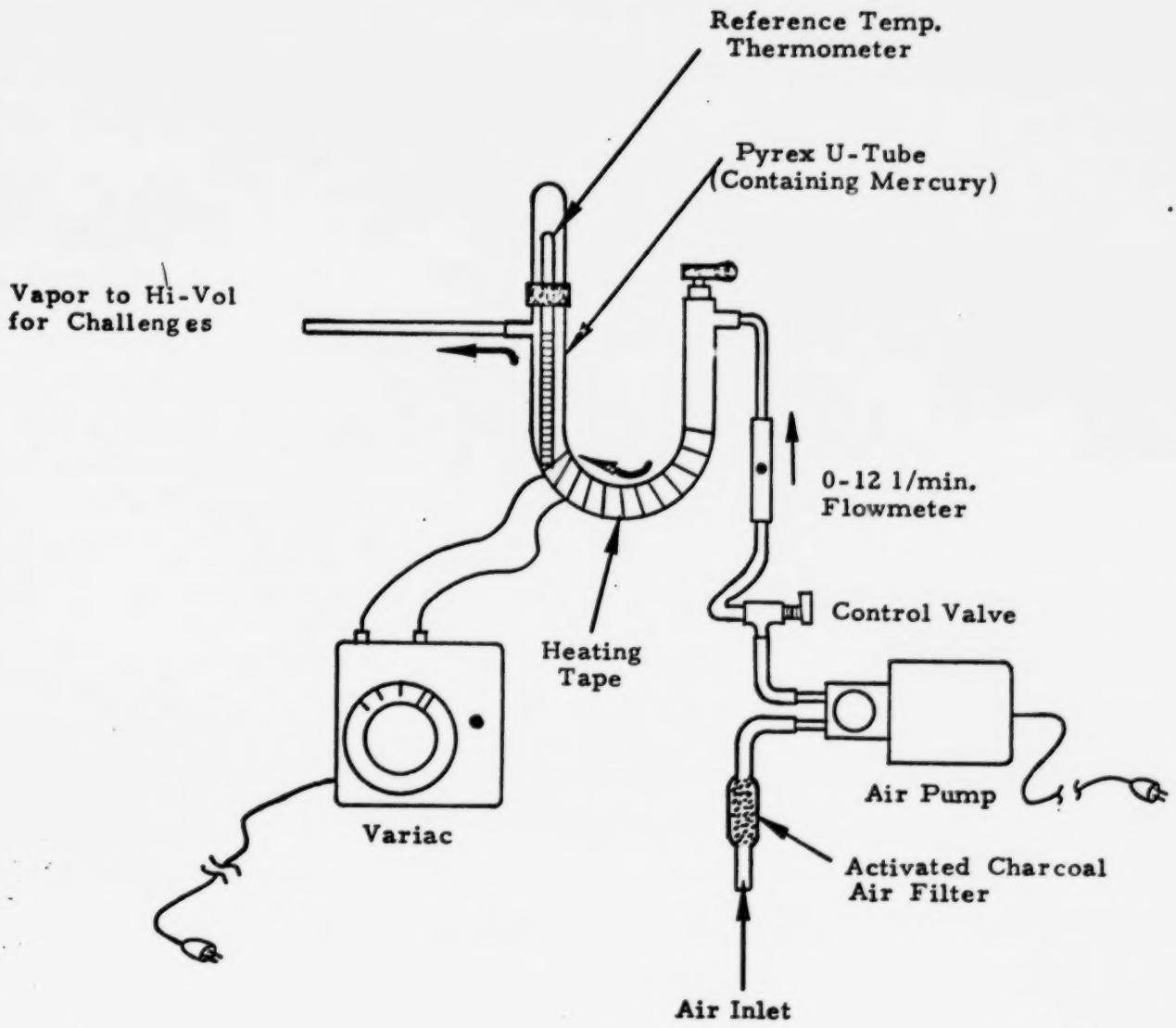


Figure 3-13 Elemental Mercury Vapor Source

Mercury vapor levels from this source were controlled by adjustment of power to a heating tape placed around the U tube. (4) Air flow through the canister was measured by use of a differential pressure gage with all components in position and operating within the Hi-Vol. Calibration of the flow is discussed in Section 3.2.2.

Bubblers for collection of mercury contained the following:

First bubbler: 13.5 ml volume, comprised of

0.5 ml $KMnO_4$ (0.25M)

4.0 ml HNO_3 (1:1)

9.0 ml H_2O

Second bubbler: 15.1 ml volume, containing

0.1 ml $KMnO_4$ (0.25M)

1.0 ml HNO_3 (1:1)

14 ml H_2O

In analysis of mercury, aliquots of the total bubbler volume were used. In general, 1.0, 2.0 or 5.0 ml were employed.

Dimethyl mercury was supplied to the mixing plenum of the test assembly from a bubbler which served as a vaporizer.

The procedure utilized in supplying dimethyl mercury was as follows: Prior to each test run a 10 µl volume of dimethyl mercury was diluted in methanol and 1.0 ml was placed in the bottom of a standard Smith-Greenberg bubbler. The concentration used was based on the average air concentration desired for the test and its planned duration. The estimated concentration was based on a series of trials which had demonstrated that approximately 55-60% of the dimethyl mercury placed in the vaporizer was recoverable in the source bubbler operating from Probe 1

at the top of the canister. In all operations the dimethyl mercury solution placed in the vaporizer was completely exhausted during a test. The vaporizer was placed in a constant temperature water bath to control the rate of sample evaporation. Air flow through the vaporizer was adjusted to prolong the total vaporization time so that it approached the duration of the test. However, no rate of vaporization has been estimated.

In order to avoid fluctuating air flow rates through the vaporizer an aliquot of the dimethyl mercury solution measuring no more than 1.0 ml was employed. This volume remained below the level of the nozzle in the bubbler/vaporizer, thus permitting smooth air flow.

Measurement of the quantity of dimethyl mercury placed in the vaporizer was carried out volumetrically: First, utilizing a capillary pipette, 10 μl of dimethyl mercury was added to 5.0 ml of methanol. A volume of 1.0 ml of this solution contains 5340 μg of dimethyl mercury (as Hg). This solution was generally used as the dimethyl mercury source for the tests in which levels greater than 30 $\mu g/m^3$ were desired. For the lower test levels a 0.5 ml volume of the first solution was diluted to 8.0 ml. This solution contains 334 μg/ml of dimethyl mercury as Hg. Adjustments to achieve the desired <u>average</u> air concentrations were made by adjusting the air flow rate through the bubbler.

Actual values for the concentration of dimethyl mercury (as Hg) which were used in the analyses of the data, were always based on the values obtained through the upper probe and its bubbler. This is indicated in the data tabulation under the heading of "Source Analysis".

Both bubblers used to evaluate the absorption of dimethyl mercury on charcoal contained 10.0 ml of 0.10N iodine monochloride.

The air flow rate through the upper bubbler (Probe 1) which was used to measure the input mercury level was 1.0 l/min. The lower bubbler operating from Probe 2 sampled the air coming through the absorbent at 1.5 l/min.

Although a bubbler sample was taken after the canister absorbent at Probe 2, for every test run, no evidence of any dimethyl mercury was obtained in any of these bubblers. Thus, within the limits of detection of mercury in this modified Hatch and Ott method, it may be stated with complete confidence that the dimethyl mercury was quantitatively absorbed by the charcoal.

The procedures utilized in analysis of the results of the tests are outlined in Sections 3.3, 3.4 and 3.6. All analyses were calibrated against controls comprising the same silver-alumina and charcoal absorbents to which controlled volumes of mercury-containing vapors were added in closed containers. The full analytical procedure was then carried out on these synthetically prepared samples.

3.2.2 Canister Air Flow Calibration

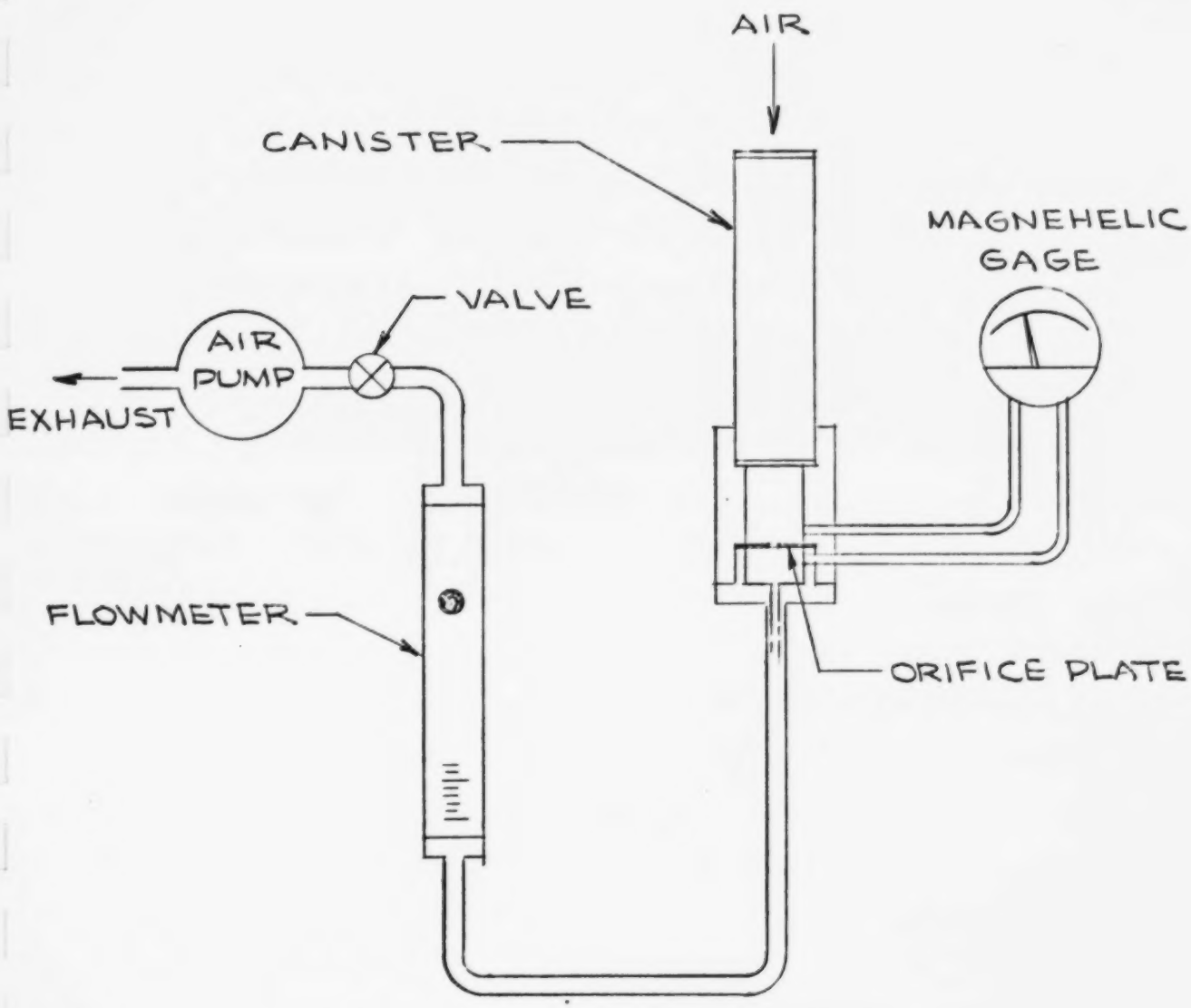
Independent calibration of air flow through the canister assembly was achieved by use of a rotameter and air pump. Figure 3-14 is a schematic of the set up.

Using the standard canister holder assembly with the 0.132 cm (.052") flow orifice in position, air was pulled through the canister and orifice opening by use of a separate air pump. The pressure drop across the opening was measured by a Magnehelic gage* with a 0-100

* Magnehelic Model 2100C, Dwyer Instruments, Inc. Michigan City, Indiana.

Figure 3-14

Air Flow Calibration of Canister



inches of water differential pressure range. By adjustment of the valve positioned in front of the pump easy control of the air flow rate was achieved. Air flow was measured by a rotameter*. Figure 3-15 shows typical air calibration data.

The air flow calibration achieved as indicated, was used to determine air flow through the canister for each test run. The differential pressure value as measured by the same Magnehelic gas was read at the start, finish and at hourly intervals, where appropriate, during each run. The average value was referred to the calibration chart (Figure 3-15) for determination of the average air flow rate during each test.

3.2.3. Processing of Elemental Mercury Absorbent

3.2.3.1 Analysis of Elemental Mercury

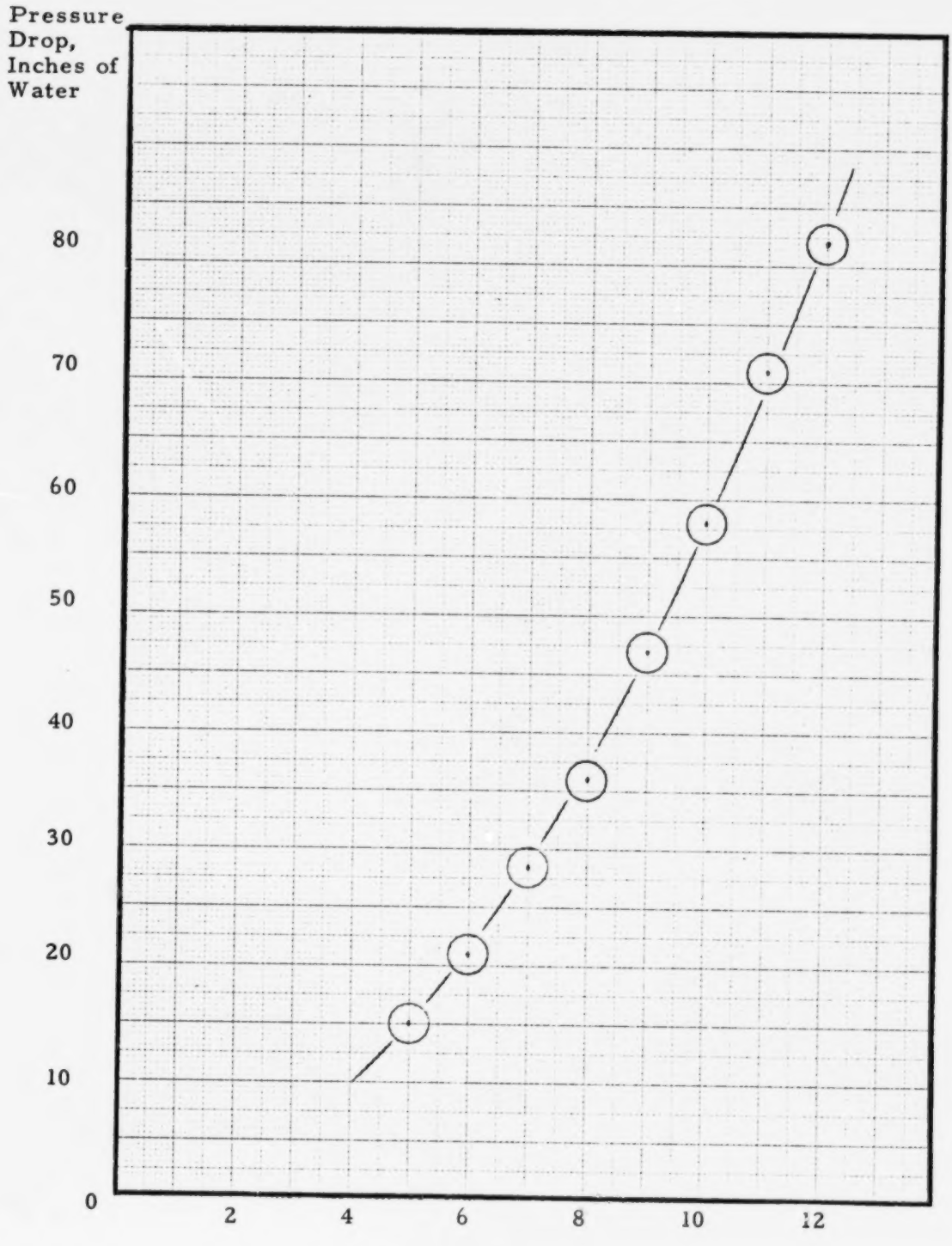
A number of methods were tested for analysis of elemental mercury after absorption on 10% silver-alumina absorbent and other absorbents. The 10% Ag/Al_2O_3 absorbent material shows capability to perform under adverse conditions which have apparently deactivated other elemental mercury absorbers. It also exhibits high capacity for mercury. Its good absorbent properties do, however, appear to make mercury recovery relatively difficult. Nevertheless, a procedure has been established which works efficiently even in the presence of contaminants. Initial efforts with contaminants such as aromatics which absorb in the wave length (253.7 nm) utilized for mercury analysis showed that a purification step was required. The following procedure was developed.

A riffled (representative) 10 gram sample of the 10% silver on alumina granules (8-14 mesh) contained in the top section of the absorbent

* Roger Gilmont Instruments, Inc.; Cat. No. F1300, Size No. 3, Air Flow Range 200-12,000 ml/min.

Figure 3-15

Calibration of Canister Air Flow



canister* were placed in a 125 ml Erlenmeyer flask. To the solid, 7.0 ml of 0.25M potassium permanganate solution and 15.0 ml of concentrated nitric acid were added. The flask was covered lightly with parafilm and agitated gently overnight on a platform shaker. If the solution is clear after shaking, the sample size was too large and the procedure should be repeated with a smaller sample, 5.0 grams. It has been found that recovery is low when the oxidizing reagents are used up.

A 5.0 ml aliquot of the extract was removed from the shaken Erlenmeyer and added to 50 ml of 1M sodium ascorbate. The metallic silver aggregated slowly; a wait of about one minute was adequate to complete precipitation. Then the silver (and mercury) was filtered out on a 25 mm disc of Whatman GF/D glass fiber held on a vacuum filter. The residue was washed with distilled water and the glass fiber and residue were transferred to a crucible** for ignition in a high frequency induction

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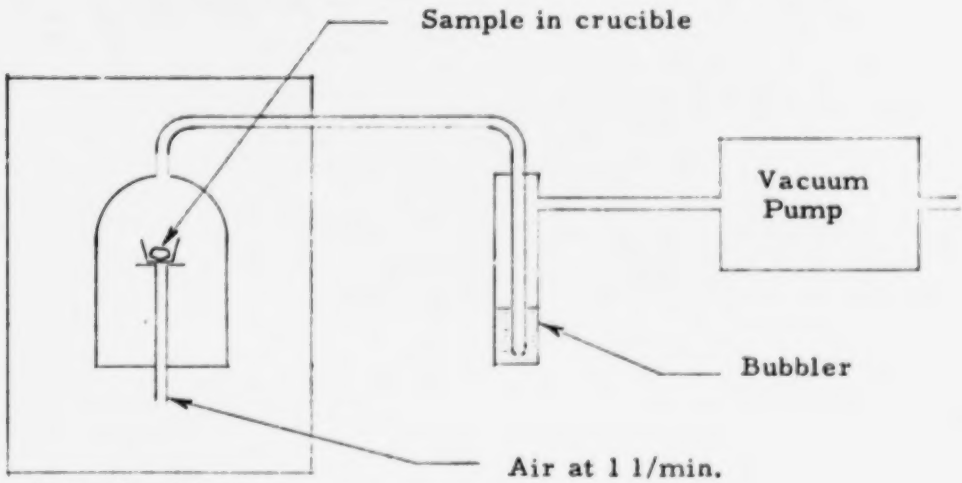
* Reference throughout is to the canister of dimensions 1" i.d. x 4-5/8" high, which contains 23.2g of 10% Ag on Al_2O_3 (23 ml) and 11.5 g (23 ml) of activated charcoal. This canister can be used at relatively high air flow rates without loss in collection efficiency. One tested sampling rate utilized is 8.0 liters/min. (hourly space velocity 20870 vol/vol-hr) which allows sampling of levels as low as 1 nanogram/m^3 in a 24 hr. day when the sampled volume is equal to 11,520 liters and the mercury collected would be 11.5 nanograms. Materials requiring longer sampling intervals cannot conveniently be sampled. This is one of the difficulties encountered with silver wool as an elemental mercury collector. It requires a low flow rate.

** A crucible such as the Leco N528-11 may be used. The induction furnace utilized was the Leco 521-000.

furnace. The following set-up was used:



Air was pulled into the induction furnace at 1.0 liter/minute. (Dry nitrogen may also be used.) The bubbler contained 9.0 ml of 1M nitric acid and 1.0 ml of 0.025 M potassium permanganate. The solid sample was heated for 3 minutes at maximum furnace grid current.

After collection of the mercury in the bubbler, 1.0 ml of 20% stannous chloride in 6N HCl was added to the bubbler. Using the same air flow, the reduced mercury was pulled through into the optical cell of the atomic absorption spectrophotometer operating in the flameless mode. Section 3.2.6 describes this operation.

The calibration data are shown in Figure 3-16. For calibration, mercury vapor was absorbed onto the solid in a clean flask which was closed by a rubber septum. Various volumes of equilibrated mercury vapor were added by hypodermic syringe to such flasks containing samples of the absorbent. The solid was then processed as indicated above. Experimental notes relative to the procedure:

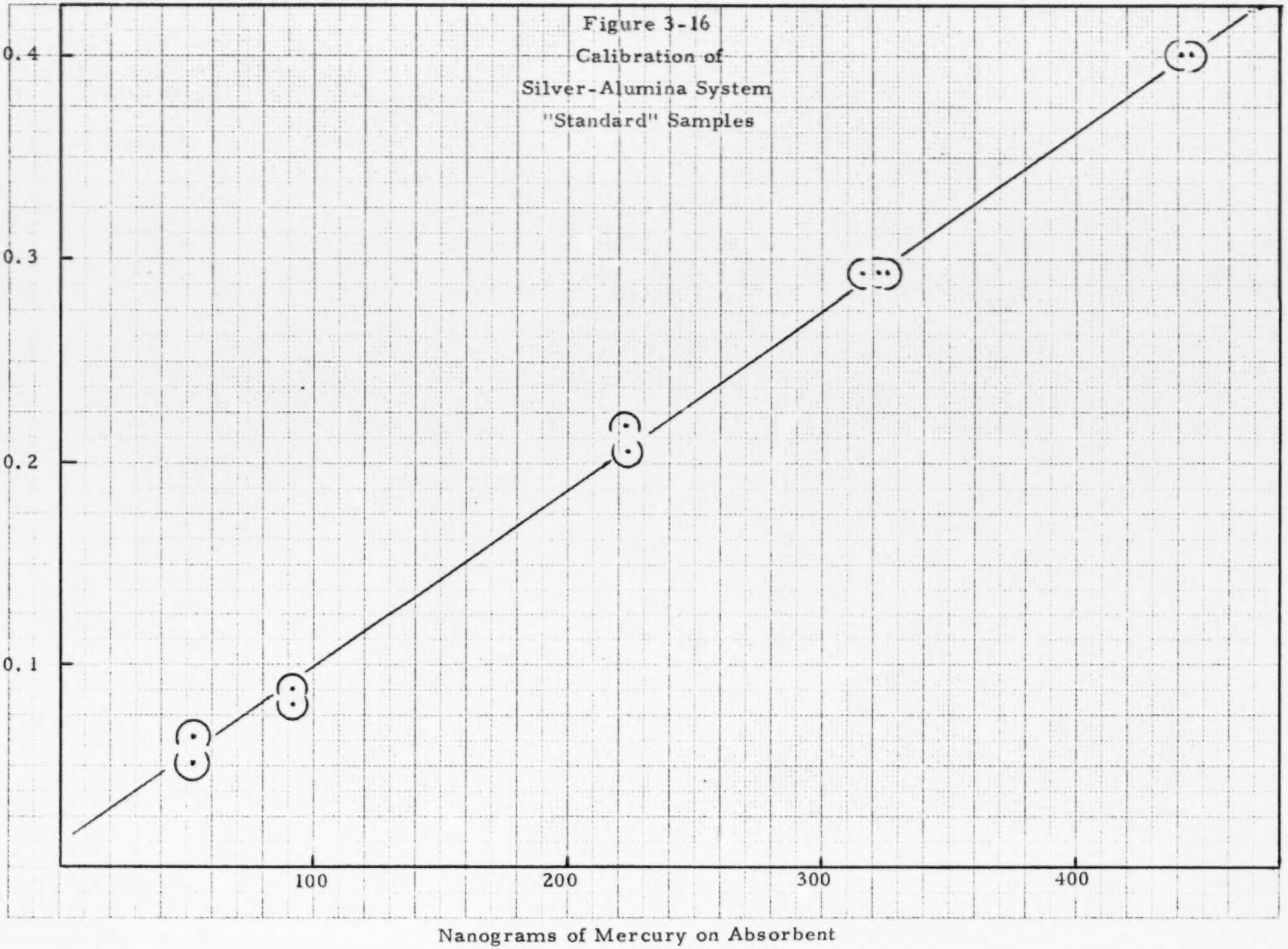


Figure 3-16
Calibration of
Silver-Alumina System
"Standard" Samples

1. Mercury in the extract obtained after treatment of the solid may be absorbed onto the manganese dioxide. Therefore it is important to mix the contents of the flask prior to removal of the aliquot used in the analysis.

2. If the aliquot taken is less than 5.0 ml, silver nitrate should be added to keep the quantity of silver on the filter relatively constant. The procedure utilized has been to add 0.2 ml of a 40% silver nitrate solution for every 1.0 ml the aliquot is below 5.0 ml. For example, if the aliquot is 3.0 ml, 0.4 ml of the 40% silver nitrate should be added. This increment is added to sodium ascorbate immediately prior to addition of the sample. By this technique, heating of the silver in the induction furnace is kept uniform from sample to sample. Variations in the amount of silver present will modify the temperature achieved.

3. Where excessive amounts of oxidizable materials have become absorbed onto the Ag/Al_2O_3 absorbent, larger volumes of the oxidizing components may be used. Calibrations have been run with 15 ml of 0.25M $KMnO_4$ and 30 ml of conc. HNO_3. Identical results were obtained.

This procedure has been qualitatively checked on addition of sulfur compounds such as H_2S, SO_2 and aromatics such as xylene to the calibration flask. Interferences were observed when the bubbler step was omitted. The bubbler process also concentrates the mercury release producing sharper absorbance peaks than would be achieved without it.

3.2.3.2 Unsuccessful Procedures

A considerable number of trial experiments were carried out in development of the specific method indicated above. Some of the less

useful attempts included:

(1) Thermal Desorption of Mercury

Typical of the problems encountered, included a trial with 450 nanograms of elemental mercury on 10 grams of silver/alumina granules. Air at 50 ml/min was pulled through a glass trap containing the sample which was supported in a resistance furnace maintained at 600-650°C. Mercury was collected in 2 bubblers each of which contained 10 ml of 0.5N HNO_3. Various periods after commencement of heating were checked. A 3 hour sample showed release of only 10-20 nanograms of mercury after 3 hours of heating. Samples collected after 6-1/2 hours of heating showed 45-50 nanograms of mercury still in the process of desorption. In addition, the glass showed considerable softening.

It may be concluded that standard resistance furnace heating of mercury on silver-alumina absorbent does not bring about sufficiently rapid desorption of the mercury for use in a short analytical procedure.

(2) Nitric Acid Extraction

A considerable variety of procedures were examined in attempts to avoid heating to desorb the mercury. For example, the silver was removed from the granules with HNO_3 and an aliquot was reduced with $SnCl_2$ and tested directly. Silver precipitated in the reduction step appeared to hold the mercury. No Hg vapor emission resulted. No other liquid extraction was found to work effectively.

3.2.4 Processing of Combined (Organic) Mercury Absorbent

3.2.4.1 Introduction

In use of the two section canister collection method, the silver/alumina "absorbent" removes the elemental portion of total mercury from

sampled gases. The second section containing activated charcoal (Barneby-Cheney, TCA, 6-10 mesh) removes vapors of compounds of mercury. These latter are considered to be mainly mercury organics such as dimethyl mercury.

Analysis of the charcoal presented several problems:

(1) All combustion and high temperature procedures resulted in the release of gases which interfered with analysis in the atomic absorption spectrophotometer set at the mercury wave length, 253.7 nm.

(2) Release of the mercury compounds by direct heating in a resistance furnace was very slow (requiring about an hour for a 1 gm sample at 600-700°C) and was also accompanied by the release interfering vapors.

(3) Use of bubbler collectors containing either $KMnO_4/HNO_3$ or ICl solutions to trap the mercury after high temperature removal of the vapors from charcoal did not separate Hg from the interference. That is, use of the bubbler extract in direct Hatch and Ott type procedure showed interference still, although on a diminished scale.

The following procedure was established which circumvented the interference problems.

3.2.4.2 Analytical Procedures

Analysis of the charcoal absorbent samples was carried out as follows:

(1) The total charcoal sample was riffled carefully to separate a representative 1.0 gram sample of the solid.

(2) The charcoal sample was transferred to the combustion chamber of an induction furnace where it was heated to redness in a nitrogen atmosphere. The temperature was approximately 1000°C. The nitrogen flow rate was 1.5 l/min. Under these conditions, the mercury

absorbate was rapidly released. After approximately 7 minutes, release of mercury was complete. Figure 3-17 shows the arrangement used for combustion.

(3) The gases released during the heating are passed through a small bore alumina tube maintained at 1000°C. This step is included to complete reduction of any mercury compounds which may have been desorbed from the charcoal absorbent without alteration. A high quality alumina tube* measuring 1/16" (i.d.) x 5-3/22" (o.d.) x 18" (length) is heated in a 14" electric furnace. This small volume tube design is utilized to minimize mercury vapor hold-up.

(4) The gases from the alumina tube were passed to a $KMnO_4$-HNO_3 bubbler which removes the mercury from the gas. These bubblers contained 0.2 ml, 0.25M $KMnO_4$, 1.0 ml, 8.3 N (1:1) HNO_3 and 13.8 ml H_2O.

(5) The system was purged into the bubbler for three minutes with nitrogen prior to analysis of the contents of the bubbler.

(6) The bubbler contents were reduced with 2.0 ml of 20% $SnCl_2$ in 6N HCl. Upon addition of the stannous chloride solution, the bubbler was immediately connected to the remainder of the analytical apparatus line. Care was taken to avoid mixing the reagents until the bubbler containing the sample was reconnected to the remainder of the apparatus. Mixing was provided by passage of air at 1.0 l/min. through

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* The Alumina tube was obtained from Thermal American Fused Quartz Co. It is specified as "high purity recrystallized" alumina, nominal bore -2.0 mm, nominal wall -1.0 mm, maximum outside diameter -4.5 mm, length -375 mm.

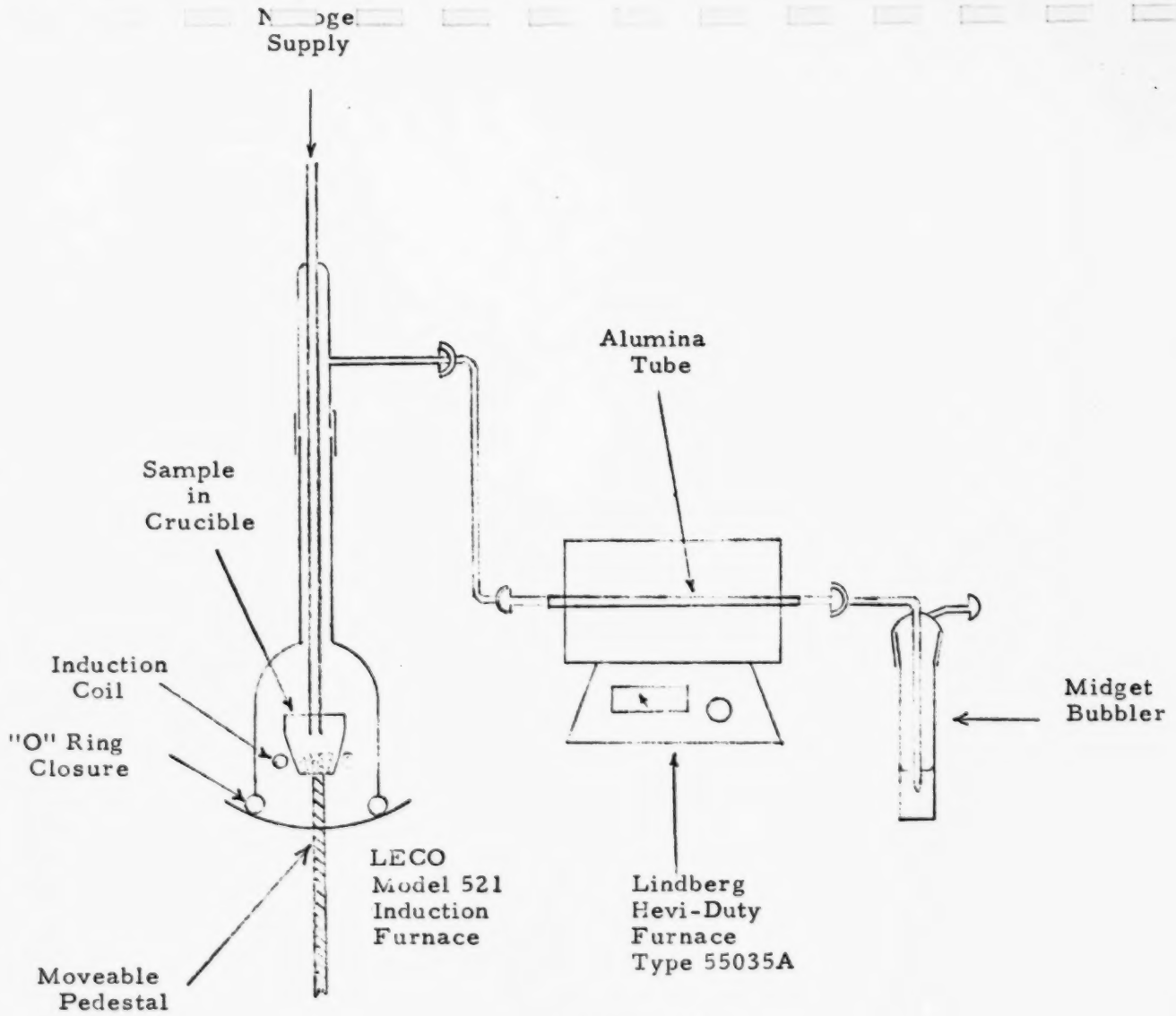


Figure 3-17

Schematic Diagram,

Charcoal Combustion System

the sample bubbler. Released vapors passed to a second bubbler containing a solution of 0.5 g sodium borohydride in 15 ml of water and thence to the optical cell in the atomic absorption spectrophotometer which quantitates the mercury vapor.

(7) Calibrations:

(a) Samples of dimethyl mercury used for quantitation with the iodine monochloride procedure were added directly to 10 ml of 0.10 N ICl in a bubbler. Freshly prepared methanol solutions of varying dilutions were used. In general, 10-40 μl volumes were used. The contents of the bubblers were then analyzed as indicated in (6). A typical calibration is shown in Figure 3-18.

(b) Calibrations of the charcoal absorbent system were carried out by the addition of dimethyl mercury (in MeOH) directly to 1.0 g of charcoal. The charcoal was then analyzed in accordance with the total procedure indicated in (1) - (6). An example of a calibration is shown in Figure 3-19 where various amounts of mercury added to charcoal samples are indicated on the abscissa, absorbance is plotted on the ordinate. The intercept is a measure of the blank value associated with charcoal samples to which no added mercury is associated.

Figure 3-18
Calibration of Dimethyl Mercury
in Iodine Monochloride Bubblers

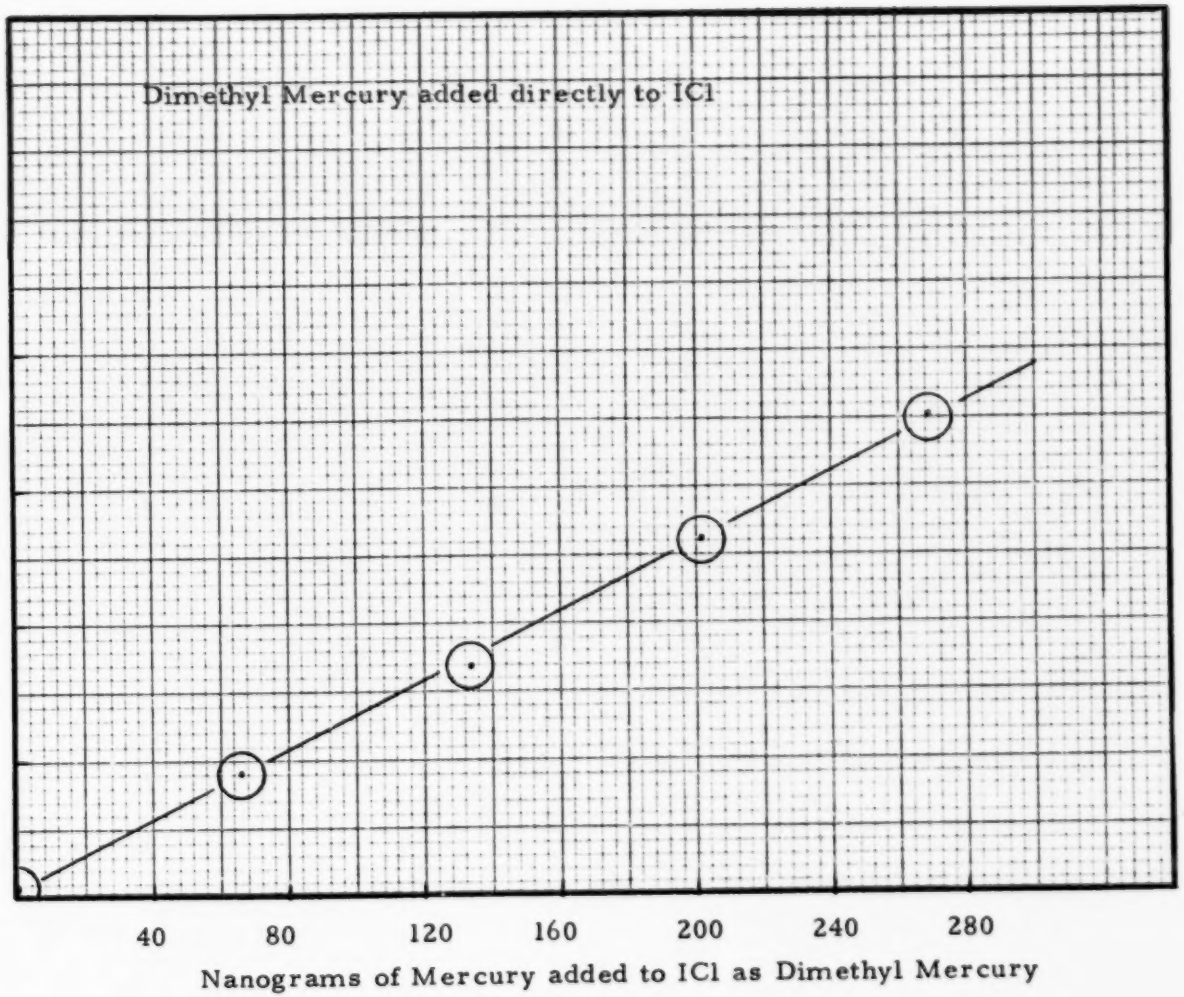
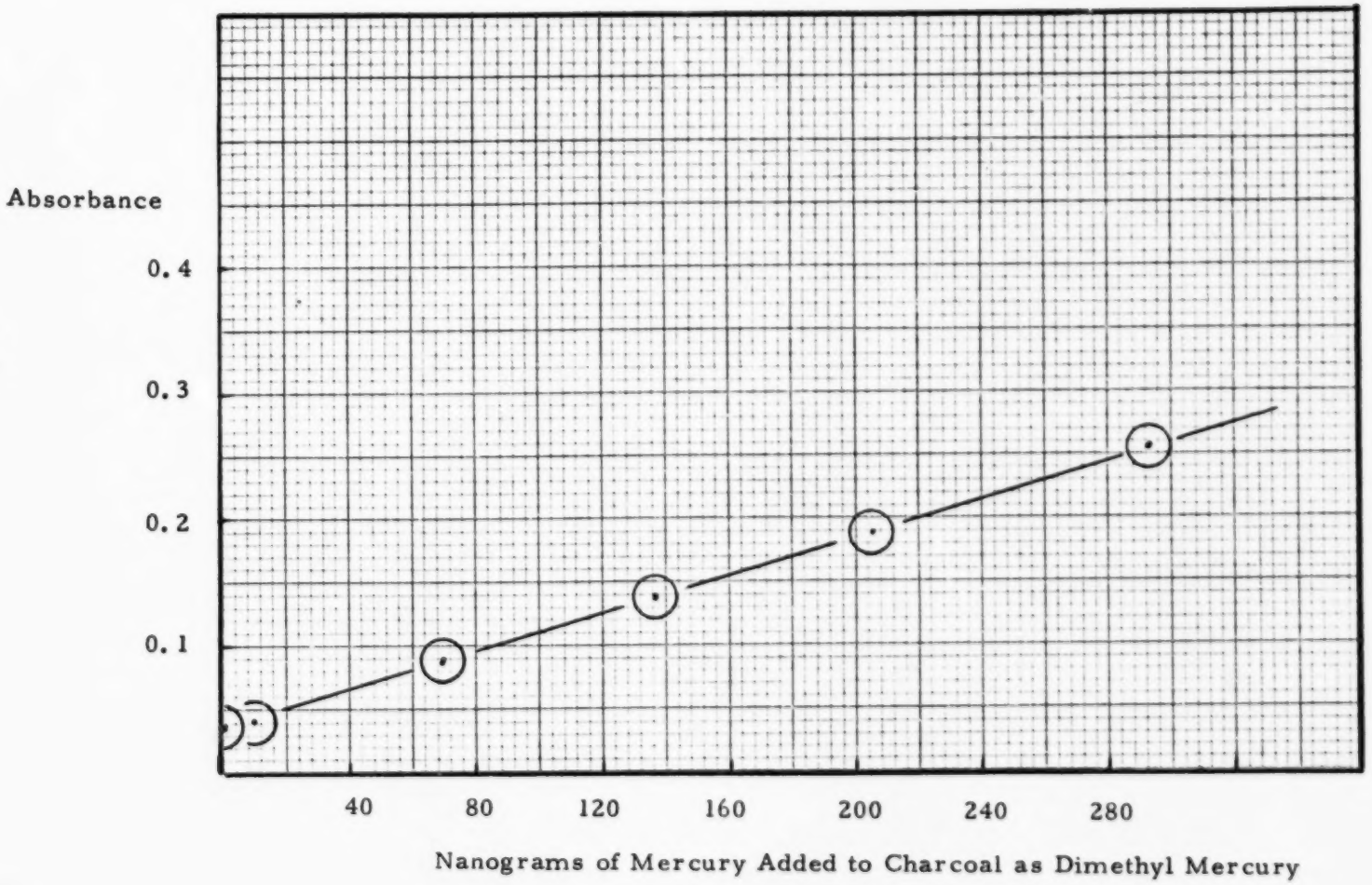


Figure 3-19
Calibration of Charcoal Absorbent System
Dimethyl Mercury Added to Charcoal



3.2.5 Processing of Particulate Samples

For testing the collection, recovery and analysis of particulates, synthetic mixtures of powdered mercuric sulfide were compounded with Cab-O-Sil (Grade M-5)*. The mixtures were homogenized in a small tube by a Vortex mixer. With the particulate filter in place in the operating collection assembly, the solid sample was vibrated into the air stream at the air inlet. Figure 3-11 shows the arrangement which was used. In general, particle preparations in which 1.0 mg of powdered HgS was mixed with 83.2 mg of Cab-O-Sil were typical of the proportion between the mercuric compound and the diluent.

After collection, the glass fiber filter was carefully removed from the collector, folded and placed in a cleaned, wide-mouth bottle which was capped and used for storage until needed: Analysis was commenced by the addition of the 35 ml of 0.25M $KMnO_4$ and 75 ml of concentrated HNO_3 to the sample on the filter. A glass stirring rod was used to break up the filter. The macerated filter-reagent mixture was allowed to sit for at least one hour after addition of the acid $KMnO_4$, when 90 ml of distilled water was added and stirred.

For analysis, a 10 ml aliquot of the liquid was removed and placed a 35 ml Greenberg-Smith impinger equipped with a standard tip. The sample was reduced with 2.0 ml of 20% $SnCl_2$ in 6 N HCl and the standard analytical determination described in the following section.

3.2.6 Analysis of Liquid Aliquots

All processed samples were analyzed by the same modified

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* Fumed Silica manufactured by the Cabot Corporation. Grade M-5 has an average particle diameter of 0.014 microns; an average surface area of 200 m^2/g.

Hatch and Ott method: (1) An aliquot of the dissolved sample was placed in a Greenberg-Smith impinger modified by use of a standard nozzle in place of impinger tip; (2) The volume was made up to 10 ml with 2N nitric acid; (3) The sample was reduced with 2.0 ml of 20% $SnCl_2$ in 6N HCl and (4) connected to a train which consists in series of a bubbler containing 10 ml of 2% sodium borohydride ($NaBH_4$), an empty impinger, an optical cell set in the optical path of a Perkin-Elmer Model 303 atomic absorption spectrophotometer, a rotameter and a vacuum pump. The arrangement is shown schematically in Figure 3-20. Air was pulled at 1-2 lpm through the system. Peak signals read as % absorption were converted to absorbance and quantitated by comparison against calibrations constructed by analysis of the various substrates.

Calibrations for each of the three main procedures which were tested, elemental mercury on Ag/Al_2O_3; $(CH_3)_2$ Hg on charcoal and HgS (Diluted) on the glass fiber filter were normally constructed end-to-end. That is, known quantities of mercury, in the appropriate form were added to the solid in the case of the absorbents, and the entire analysis was carried out with known samples to obtain a calibration for determination of unknown collector samples. Typical calibration curves have been shown in the sections which described the processing of each absorbent.

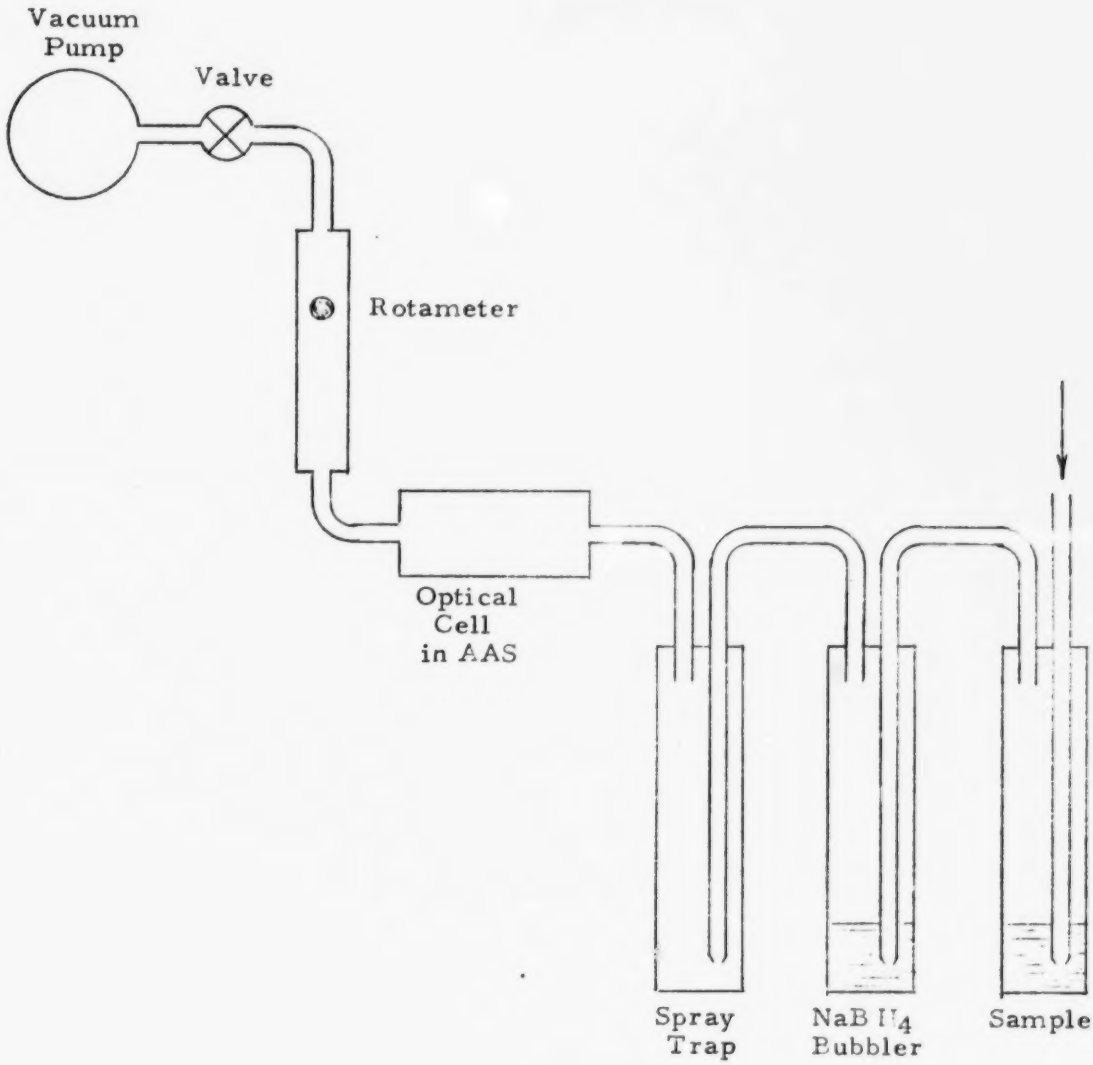
3.3 RESULTS

3.3.1 Screening Tests for Absorbents

Three absorbents were tested for suitability in elemental mercury collection by the canister method: (1) Silver wool, (2) 10% silver on alumina and (3) a silver zeolite. These materials had been demonstrated

Figure 3-20

Schematic of Analytical System



as most promising in previous tests.

The silver wool used was Baker Catalog No. V007, for micro analytical applications. It is described as silver wire, approximately 5 microns in diameter, containing not less than 99.99% silver after degreasing.

The silver-alumina absorbent was made by adding 30 ml of a silver nitrate solution which contained 0.67 g $AgNO_3$ per g H_2O to 100 g of 8-14 mesh, Alcoa F-1, activated alumina. With shaking, this solution was dripped slowly through a separatory funnel into an evacuated vacuum flask which contained the alumina. After the solution was completely added, the granules were dried at 100°C and then calcined at 700°C for several hours. The silver was not further reduced.

The silver zeolite was a 100% silver exchanged, Type 13X, 12-16 mesh, chromatographic grade molecular sieve purchased from Coast Engineering Laboratory. Its silver content is the result of completely exchanging the sodium of the zeolite by silver.

These materials were screened in simple tube (1/2" i.d.) configuration using relatively low levels of mercury vapor: 5-20 $\mu g/m^3$.

Qualitatively, the following results were obtained. The silver wool (2 grams) after cleaning and activation, collected mercury vapor efficiently at low flow rates. For example, at 200 ml/min. collection efficiency was excellent and no mercury was detected passing to the detector positioned below the test bed. At 400 ml/minute, 2-5% of the mercury was detectable. At higher flow rates, larger percentages passed the absorbent. A simple calculation for ambient levels, i.e. 5 nanograms/m^3

indicates that very long runs would be required at the effective flow rates to utilize silver wool. To collect 5 nanograms, a detectable quantity by an atomic absorption spectrophotometer, a 5000 minute collection cycle would be required. Even a tenfold improvement in collection parameters such as by use of a 20g sample in a half-canister configuration, would probably not be adequate to qualify silver wool for use in the projected operations. Therefore, testing with wool was discontinued.

A ten gram portion of the 10% silver on Alcoa alumina preparation was tested similarly, initially. It passed no mercury at flow rates up to 10 liters per minute in the laboratory screening device.

The silver zeolite was technically a most promising material. It collected mercury as effectively as the Ag/Al_2O_3 preparation. However, its particle size (12-16 mesh) made achievement of 1-2 l/min flow rates difficult. In analysis of the solid, however, the zeolite held tenaciously to its silver and mercury. At all levels of mercury complete recovery proved impossible to achieve. Testing of the zeolite was discontinued.

Considerations in terms of equal quantities of silver shows that the 10% silver/alumina absorbent is vastly superior to silver wool. A 24g canister charge of Ag/Al_2O_3 contains approximately 2.4g of silver. A silver wool packing for a canister requires approximately 15g of silver as a minimum. The latter still requires operation at low air throughputs.

In addition, screening tests of the silver/alumina absorbent showed complete passage of dimethyl mercury vapor without measurable retention. Thus, it exhibited the selectivity required for the top section of the two part canister absorber. On the basis of the three materials screened, the 10% silver on alumina was selected for more complete

testing in the canister and High-Volume sampler.

Previous testing of the Barneby-Cheney TCA Grade charcoal had shown this material to have the desired properties for an absorber of organic mercury compounds. It fully removes organic mercury vapors as exemplified by dimethyl mercury under the desired flow parameters. It does not collect elemental mercury as demonstrated in laboratory screening tests. In addition, it is the only charcoal tested which can be heated directly in the Leco induction furnace. On the basis of these properties, the TCA Grade charcoal was selected for use in the lower section of the canister absorber.

3.3.2 Elemental Mercury Collection Tests

Tests of the 10% silver on alumina absorbent were run with synthetically generated mercury vapor concentrations ranging from the ambient level in the laboratory to approximately 200 $\mu g/m^3$. Those utilizing the ambient level were run over 5 to 6 hour intervals; all others were run for one hour. Analyses were run in duplicate or in triplicate. That is, aliquots of the riffled solid absorbent, 3-10g each, were run separately to obtain reasonable agreement. Separate calibrations were run for each day. Bubbler samples which determined the elemental mercury level in the source were analyzed in the same way as those resulting from induction furnace heating, followed by collection in $KMnO_4$-HNO_3 bubblers.

The data for test runs at elemental mercury vapor concentrations ranging from 0.044 to 201 $\mu g/m^3$ are collected in Table 1. The High-Volume air sampler was operated in the range 24.0-24.8 CFM for these tests. The sample air through the canister was controlled at 9.8 lpm.

Table 1

Collection of Elemental Mercury on 10% Silver-Alumina Granules

Duration (min.)	Elem. Mercury Canister Anal. ($\mu g/m^3$)	Elem. Mercury Aver. Value Canister Anal. ($\mu g/m^3$)	High-Vol. Average Air Sample Rate (CFM)	Source Bubbler Anal. ($\mu g/m^3$)	Sample Air Vol (liters)	Air Sample Humidity (RH)	Sample Temp. (^oF)	% Recovery
60	1.98 2.50 1.54	2.0	24.8	1.19	590	35	75	168
60	2.09 1.76	1.9	24.7	1.36	590	38	77.5	140
60	1.92 2.50 2.37	2.3	24.5	2.62	590	42	79.5	88
60	2.75 1.92 2.69 1.85	2.3	24.0	2.56	590	28	81	90
60	8.51 9.55	9.0	24.0	10.3	590	30	74	87
60	8.73 10.43	9.6	24.0	10.3	590	32	74	92
60	118 118	118	24.0	111	590	52	76	106
60	201 201	201	24.0	188	590	58	78	107
392	0.044	0.044	24.0	0.055	3840	62	76	80
343	0.049	0.049	24.0	0.058	3360	57	75	84
						Average		104 %
						%Standard Deviation		± 18.8%

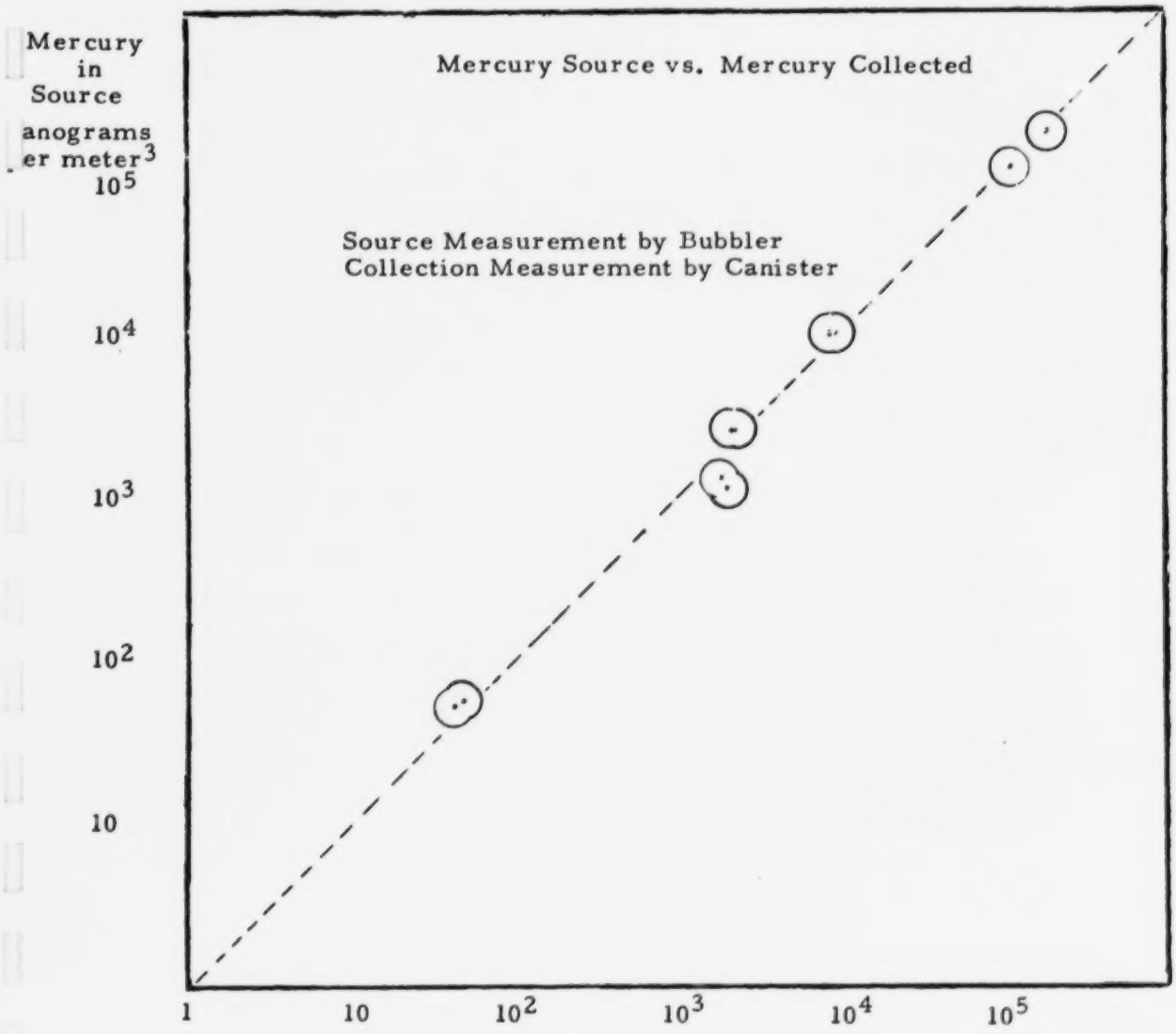
The column labelled Source Bubbler Anal. refers to the results obtained in analysis of the bubbler which extracted air at 1.0 lpm from the stream immediately prior to its entry into the canister sampler. In all cases the sample obtained from the bubbler located below the canister was indistinguishable from the reagent-absorbent blank. Thus, it may be concluded that the canisters were, within the limits of the analytical procedure, 100% efficien' in extraction of mercury from air under the conditions of these experiments.

More prccisely, the reagent-absorbent blank was equal to 1-2 divisions on the strip chart of the atomic absorptior spectrophotometer. The system response to the samples obtained from the No. 2 bubbler was not greater than that blank, or the mercury equivalent of a few nanograms/meter^3 of air. This value was constant regardless of the level of the mercury in the air sample.

Figure 3-21 shows the results of these runs plotted on a log-log scale. The ordinate units are the results obtained from analysis of the bubbler contents sampled at the top of the absorbent canisters. The abscissa shows the results obtained from analyses of the canister absorbents. That is, the air concentrations sampled and analyzed extended from approximately 40 nanograms of mercury/meter^3 to 200 micrograms/meter^3. The diagonal dotted line shows the theoretical equivalence of these data. The recovery averaged 104% with a standard deviation of $\pm$ 18.8%. The high values of the standard deviation are generally attributable to values obtained at the lower levels of mercury vapor concentration. In evaluation of these data it should be recognized that a finite estimate of probable error is associated with each of the coordinates.

Figure 3-21

Collection of Elemental Mercury by Absorbent Canister



On the basis of these data, it may be concluded that 10% silver on alumina is an effective collector of elemental mercury over the full range of mercury concentrations near ambient to 200 $\mu g/m^3$.

3.3.3 Collection of Dimethyl Mercury

Tests for collection of mercury organic compounds were run with dimethyl mercury. The absorbent tested was charcoal, Barneby-Cheney, TCA Grade. Synthetic samples were generated in the laboratory as indicated in Section 3.2. Laboratory samples were varied from 0.57 to 113.2 $\mu g/m^3$ (as Hg) in concentration. Collection intervals varied from 7 to 207 minutes in these tests. Analyses of the solid absorbents were all run in duplicate. The bubbler samples taken at Probe 1 (Figure 3-11) were also analyzed in duplicate. The average value of the mercury trapped by these iodine monochloride bubblers is included in Table 2, which summarizes the operating parameters and the results obtained.

The results of the tests have been represented in Figure 3-22 with a log-log plot of the canister concentrations plotted against the results obtained from the source bubbler sample taken above the canister. The results for the data fall appropriately on the 45° line indicating no noticeable bias in collection of organic mercury in either the ICl bubbler or the charcoal. The average recovery of dimethyl mercury was 96.3%; the standard deviation of the recovery was $\pm$ 11.5%.

If the runs at (CH_3) Hg levels >1 $\mu g/m^3$ are considered exclusively, the collection efficiency defined as

$$\frac{\text{Recovery of } (CH_3)2 \text{ Hg from charcoal}}{\text{Recovery of } (CH_3)2 \text{ Hg from source bubbler}} \times 100\%$$

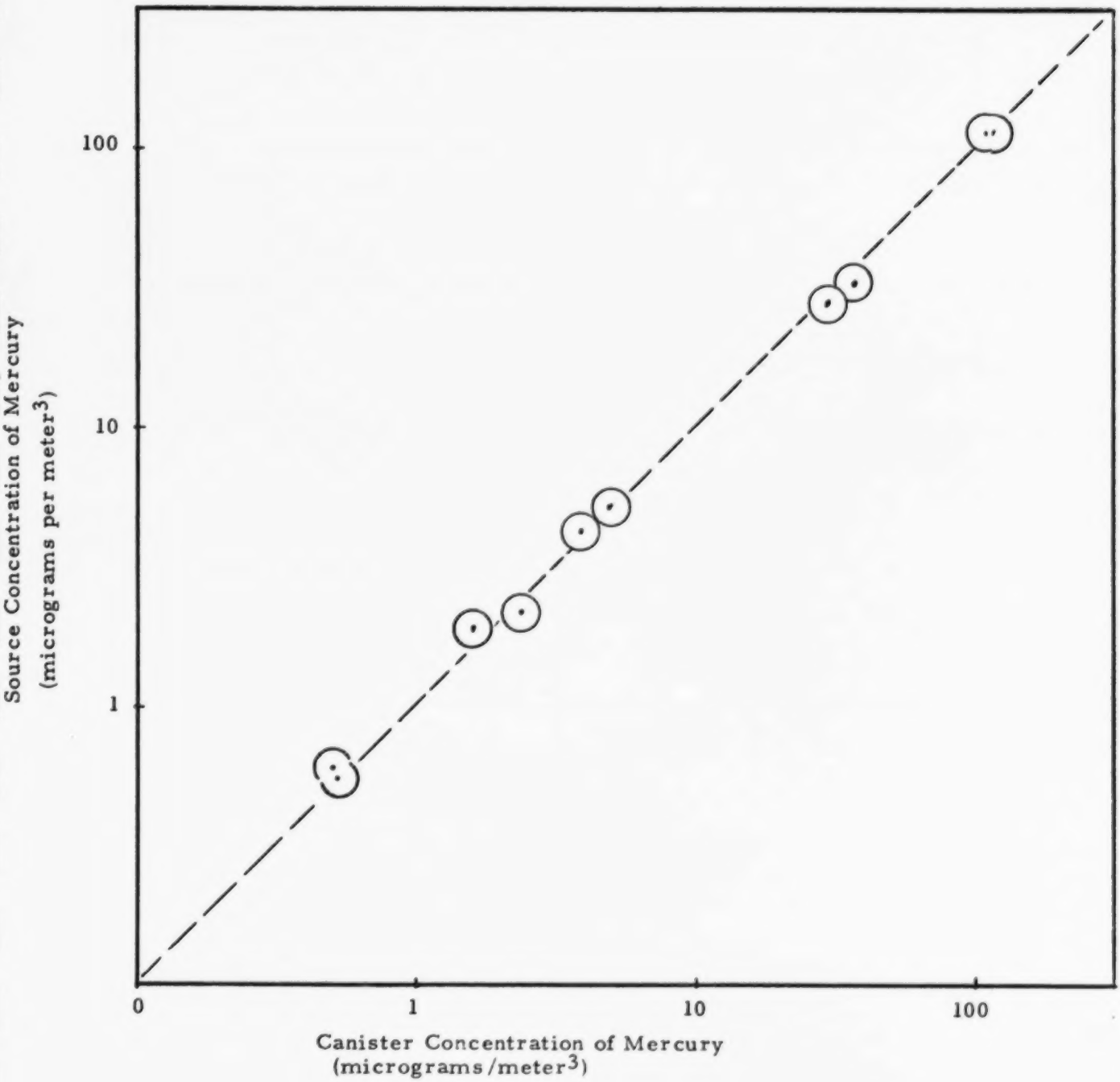
Table 2
Collection of Dimethyl Mercury

Duration (min)	Organic Mercury Analysis: Individual Tests ($\mu g/m^3$)	Organic Mercury Analysis: Average ($\mu g/m^3$)	Average Total Air Sampling Rate(CFM)	Average Canister Air Sampling Rate (l/min)	Air Sample Temp (°F)	Air Sample Humidity (RH)	Source Analysis ($\mu g/m^3$)	% Recovery	Source Air Flow Rate (ml/min)
10	29.8 31.2	30.5	24.0	9.5	73	33	28.4	107.4	400
7	4.4 5.2	4.8	24.0	9.5	71	35	5.1	94.1	400
8	35.0 38.4	36.7	24.0	9.5	73	35	32.5	112.9	400
26	3.8 3.8	3.8	24.0	9.5	74	35	4.3	88.4	100
37	2.4 2.4	2.4	24.0	9.5	71	41	2.2	109.1	60
41	105.0 115.8	110.4	24.0	9.5	77	42	113.2	97.5	60
45	114.9 114.9	114.9	24.0	9.5	70	51	111.1	103.4	60
95	1.48 1.74	1.61	24.0	9.5	77	48	1.82	83.9	40
139	0.42 0.54	0.48	24.0	9.5	78	46	0.60	80.0	60
207	0.42 0.56	0.49	24.0	9.5	75	51	0.57	86.0	20

Average Recovery 96.3%

% Standard Deviation 11.4%

Figure 3-22
Collection of Dimethyl Mercury on Charcoal



averages 100.1%. However, the standard deviation for the recovery is ± 9.9%. The two determinations obtained at levels less than 1 $\mu g/m^3$ showed lower recoveries.

In all of the tests indicated, dimethyl mercury collection was quantitated from the charcoal section of canisters which contained both absorbents. That is, the 10% Ag/Al_2O_3 absorbent and the TCA charcoal were both exposed to the dimethyl mercury vapor in that order. Thus, the results also indicate that the absorber for elemental mercury does not extract dimethyl mercury from the gas stream.

On the basis of these data it may be concluded that TCA Grade charcoal is an effective absorber for organic mercury (Dimethyl mercury) vapors over a range of concentrations from ambient to those in excess of 100 $\mu g/m^3$. Silver on alumina is not active in extraction of mercury organics as exemplified by collection of dimethyl mercury from air streams.

3.3.4 Collection of Particulate Mercury

Laboratory collection tests for particulate mercury were carried out with powdered mercuric sulfide diluted in Cab-O-Sil. The experimental technique has been indicated in Section 3.2.5.

Tests varied in duration from 10 minutes to one hour under conditions where the total final particle loading on the glass fiber filter varied from 2610 to 19200 µg on the basis of the weight of charge released into the collector air stream. This is equivalent to a particle concentration range of 384.2 $\mu g/m^3$ to 471.1 $\mu g/m^3$. In terms of HgS (as Hg) the particle loading on the filters varied from 31 µg to 228 µg or 4.56 to 5.59 $\mu g/m^3$ of air. During all experiments, the High-Volume sampler was operated at 24 CFM.

Individual run data are collected in Table 3. A plot of charge weight vs. recovery has been constructed as Figure 3-23. Recoveries for the tests were centered about the 45° theoretical recovery line, indicating no experimental bias in the method. Recovery of mercuric sulfide (as Hg) for the tests averaged 101% with a standard deviation of $\pm$ 5.1%.

On the basis of the results, it may be concluded that low-level mercury particulate concentrations are determinable by use of the High-Volume air sampler and the analytical methods outlined in Section 3.2.

Table 3

Collection of Particulate Mercuric Sulfide

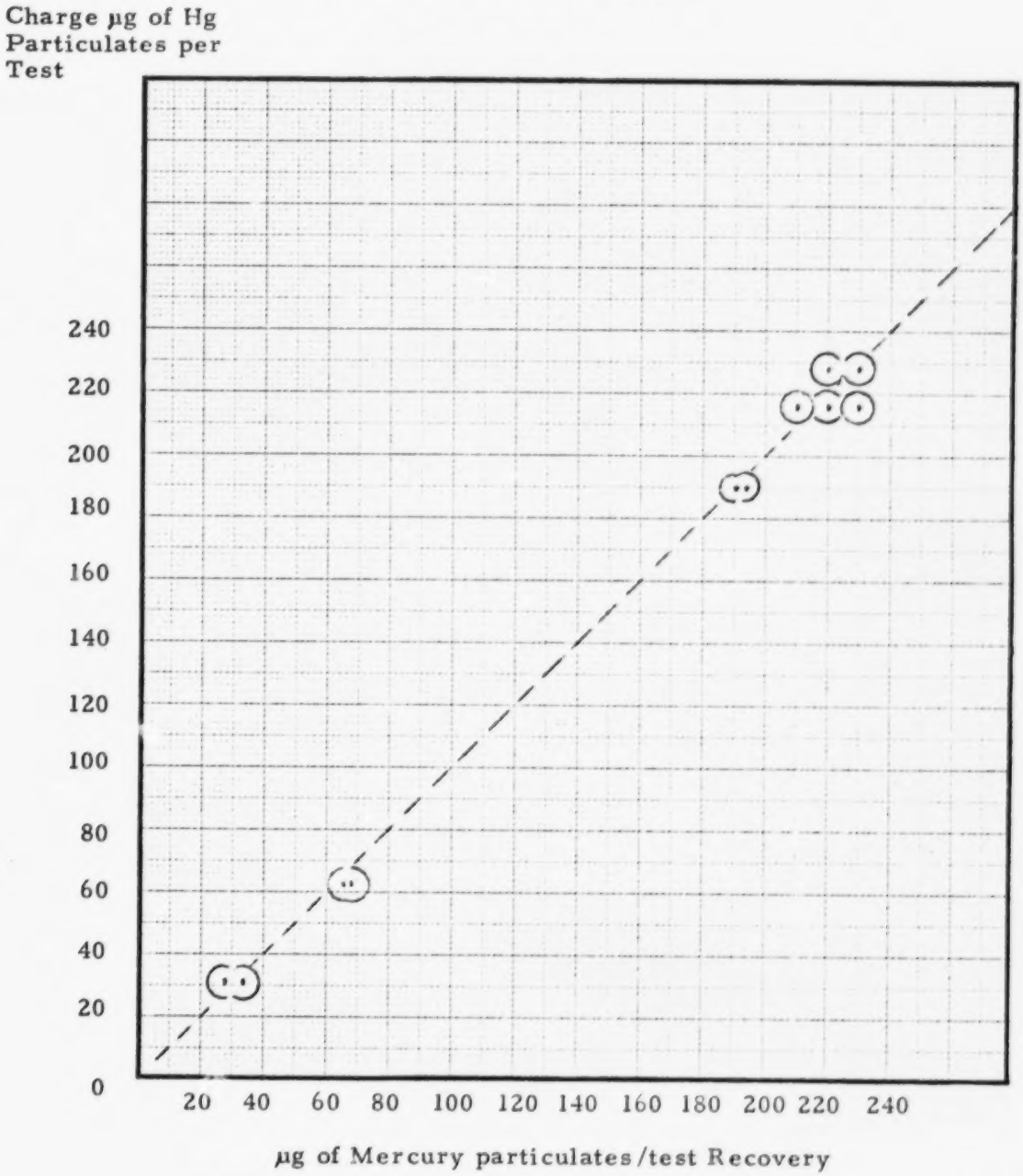
Duration (min.)	High - Vol Average Air Sample Rate (CFM)	Total Particulate Charge to Filter (µg)	Particulate Charge as Hg (µg)	Temp. (°F)	Humidity (RH)	Recovery (µg-Hg)	Collection Efficiency (%)
10	24.0	2610	31	72	35	29	94
10	24.0	2610	31	72	38	34	110
25	24.0	5305	63	75	42	66	105
25	24.0	5305	63	74	43	68	108
60	24.0	16000	190	72	52	194	102
60	24.0	16000	190	73	55	192	101
60	24.0	18270	217	73	57	210	97
60	24.0	18270	217	75	60	220	101
60	24.0	18270	217	74	48	230	106
60	24.0	19200	228	72	49	230	101
60	24.0	19200	228	70	50	230	101
	-	0	Blank	-		1	
					Average Coll. Eff.		101%
					% Standard Deviation		4.9%

Figure 3-23

Collection of Particulate Mercury

on

Glass Fiber Filters



3.3.5 Tests for Effects by Interferences

3.3.5.1 Introduction

Tests for the effects of interferences were carried out utilizing simultaneous collection of elemental and dimethyl mercury from synthetically generated inputs. In addition, the candidate interferences, hydrogen sulfide, sulfur dioxide and nitrogen dioxide were metered in at concentrations of 1.2, 5.0 and 3.2 PPM, respectively.

In the conduct of these experiments, initial tests were run with two bubblers monitoring the inlet gases at the position of Probe 1 in Figure 3-11. That is, a bubbler containing 0.1N iodine monochloride was set up to sample for total mercury in the air stream, while the nitric acid-permanganate bubbler was installed for measurement of elemental mercury input. It became rapidly apparent that canister recoveries based on analyses of the iodine monochloride bubblers were too high, leading to the not surprising conclusion that the performance of iodine monochloride as a collection medium particularly in the presence of SO_2 was erratic. Thus, another procedure for calibrating the input of elemental mercury and dimethyl mercury in the presence of the added, interfering gases was devised. Basically, it consisted of setting up separate experiments with each of the vapor sources while excluding the interfering gases and the canister collectors from the apparatus. Thus, at least four determinations of the inputs of elemental mercury and dimethyl mercury were made separately under each set of conditions planned for the interference tests. Dimethyl mercury was determined by analysis of the iodine monochloride collector. For the analysis of elemental mercury, the acidic permanganate medium was used. For elemental mercury the vapor

concentration was adjusted by varying the temperature of the vaporizer/generator (Figure 3-13). Dimethyl mercury was varied by addition of methanol solutions of varying concentrations to the source bubbler (Page 3-21). The average values obtained under the appropriate set of generator conditions were recorded as the vapor source concentration. In Tables 4, 5 and 6 the columns headed, "Organic Mercury Source" and "Elemental Mercury Source" contain the vapor concentrations determined prior to the test with the interferences.

3.3.5.2 Effects of Hydrogen Sulfide

The data obtained in a series of tests of collection of elemental mercury and dimethyl mercury by the canister method in the presence of 1.2 PPM hydrogen sulfide are tabulated in Table 4. Tests were conducted for 46-50 minutes under flow conditions of 24 CFM through the Hi-Vol sampler. Of the total air flow 8.0 lpm was diverted through the canister collectors. Dimethyl mercury-elemental mercury concentration pairs which were used were (1) 1.75 $\mu g/m^3$ $(CH_3)_2$ Hg with 2.2 $\mu g/m^3$ elemental mercury, (2) 3.75 $\mu g/m^2$ $(CH_3)_2$ Hg with 10.5 $\mu g/m^3$ elemental Hg and (3) 44.5 $\mu g/m^3$ $(CH_3)_2$ Hg with 300 $\mu g/m^3$ elemental mercury. These three pairs of concentrations were tested four times each.

The twelve tests evidenced an average recovery of total mercury from both sources of 98.2% ($\sigma = \pm 5.0\%$). Elemental mercury recovery was 99.6% ($\sigma = \pm 6.1\%$). Dimethyl mercury recovery was 92.8% ($\sigma = \pm 6.0\%$). From these data it may be concluded that the presence of hydrogen sulfide is without effect on the collection of elemental mercury by the silver/alumina absorbent. The significance of the slightly low recovery of dimethyl mercury on charcoal is not determinable.

Table 4

Collection of Elemental and Organic Mercury in Presence of 1.2PPM Hydrogen Sulfide

Duration (min.)	Average Air Sampling Rate Hi-Vol (CFM)	Canister Air Sampling Rate (lpm)	Air Sample Humidity (RH)	Air Sample Temp. (°F)	ICl Source Bubbler Anal ($\mu g/m^3$)	$KMnO_4$-HNO_3 Bubbler Anal ($\mu g/m^3$)	Organic Hg Source ($\mu g/m^3$)	Elem Hg Source ($\mu g/m^3$)	Canister Analysis Elem Hg ($\mu g/m^3$)	Canister Analysis Organic Hg ($\mu g/m^3$)	% Recovery (Total)	% Recovery (Elemental)	% Recovery (Organic)
50	24.0	8.0	38%	72°F	3.52	-	1.75	2.2	2.06	1.66	94.2	93.6	94.8
50	24.0	8.0	40	70	3.52	-	1.75	2.2	2.42	1.66	103.2	110.0	94.8
50	24.0	8.0	38	73	3.40	-	1.75	2.2	2.06	1.59	94.2	92.4	90.9
50	24.0	8.0	36	71	3.47	-	1.75	2.2	2.22	1.65	98.0	100.9	94.3
47	24.0	8.0	39	77	13.5	-	3.75	10.5	10.8	3.70	101.8	102.9	98.7
47	24.0	8.0	40	76	15.1	-	3.75	10.5	10.7	3.62	101.2	101.9	96.5
47	24.0	8.0	42	75	10.0	-	3.75	10.5	9.9	3.40	93.3	94.3	90.7
47	24.0	8.0	44	73	10.6	-	3.75	10.5	10.4	3.53	97.8	99.0	94.1
46	24.0	8.0	45	75	356.5	327.7	44.5	300	311.6	38.2	101.5	103.9	85.8
46	24.0	8.0	42	74	339.1	308.2	44.5	300	325.4	46.3	107.9	108.5	104.0
46	24.0	8.0	48	72	277.2	277.2	44.5	300	273.8	38.2	90.6	91.3	85.8
46	24.0	8.0	46	75	202.2	281.1	44.5	300	289.2	36.7	94.6	96.4	82.5
									Average % Recovery		98.2	99.6	92.8
									Standard Deviation		5.0	6.1	6.0

Table 5

Collection of Elemental and Organic Mercury in Presence of 5.0PPM SO_2

Duration (min.)	Average Air Sampling Rate Hi-Vol (CFM)	Canister Air Sampling Rate (lpm)	Air Sample Humidity (RH)	Air Sample Temp. (°F)	ICl Source Bubbler Anal ($\mu g/m^3$)	$KMnO_4$ HNO_3 Bubbler Anal ($\mu g/m^3$)	Organic Hg Source ($\mu g/m^3$)	Elem Hg Source ($\mu g/m^3$)	Canister Analysis Elem Hg ($\mu g/m^3$)	Canister Analysis Organic Hg ($\mu g/m^3$)	% Recovery (Total)	% Recovery (Elemental)	% Recovery (Organic)
55	24.0	8.0	41%	71°F	5.96	3.53	1.93	3.7	3.59	2.02	99.6	97.0	104.7
55	24.0	8.0	38	74	5.59	3.75	1.93	3.7	4.14	1.93	107.8	111.9	100.0
55	24.0	8.0	40	72	2.91	2.47	1.93	3.7	3.26	1.76	89.2	88.1	91.2
55	24.0	8.0	42	72	2.73	2.52	1.93	3.7	3.65	1.98	100.0	98.6	102.6
44	24.0	8.0	36	76	377.3	303.4	46.7	300	333.0	55.4	112.0	111.0	118.6
44	24.0	8.0	39	78	359.1	276.1	46.7	300	324.0	51.7	108.4	108.0	110.7
44	24.0	8.0	42	72	231.8	204.5	46.7	300	270.0	43.7	90.5	90.0	93.6
44	24.0	8.0	37	74	211.4	177.3	46.7	300	257.4	51.7	89.1	85.8	110.7
									Average % Recovery		99.6	98.8	104.0
									Standard Deviation		9.3	10.5	9.2

Table 6

Collection of Elemental and Organic Mercury in Presence of 3.2PPM NO_2

Duration (min.)	Average Air Sampling Rate Hi-Vol (CFM)	Canister Air Sampling Rate (lpm)	Air Sample Humidity (RH)	Air Sample Temp (°F)	ICl Source Bubbler Anal ($\mu g/m^3$)	$KMnO_4$ HNO_3 Bubbler Anal ($\mu g/m^3$)	Organic Hg Source ($\mu g/m^3$)	Elem Hg Source ($\mu g/m^3$)	Canister Analysis Elem Hg ($\mu g/m^3$)	Organic Hg ($\mu g/m^3$)	% Recovery (Total)	% Recovery (Elemental)	% Recovery (Organic)
45	24.0	8.0	38	76°F	8.00	6.04	1.94	6.6	6.22	1.89	95.0	94.2	97.4
45	24.0	8.0	42	74	8.50	6.98	1.94	6.6	6.92	1.89	103.2	104.8	97.4
45	24.0	8.0	45	77	8.10	6.20	1.94	6.6	6.45	1.87	97.4	97.7	96.4
45	24.0	8.0	46	71	8.72	6.42	1.94	6.6	6.64	1.67	97.3	100.6	86.1
45	24.0	8.0	45	75	357.8	316.7	45.3	300	318.6	47.4	106.0	106.2	104.6
45	24.0	8.0	47	73	382.2	323.3	45.3	300	325.6	54.2	110.0	108.5	119.6
45	24.0	8.0	48	77	335.5	300.0	45.3	300	295.7	44.3	98.5	98.6	97.8
45	24.0	8.0	36	79	345.5	296.7	45.3	300	298.7	47.4	100.2	99.6	104.6
									Average % Recovery		101.0	101.3	100.5
									Standard Deviation		5.1	4.8	9.6

Tentatively, a small inhibiting effect may be indicated by this result; on the basis of the SO_2 and NO_2 results, the low (92.8% $\pm$ 6.0%) result appears more probably an artifact of the experimental techniques.

3.3.5.3 Effects of Sulfur Dioxide

A series of tests, similar to those run to test the collection of elemental mercury on 10% silver on alumina and dimethyl mercury on Barneby-Cheney TCA activated charcoal, respectively, in the presence of hydrogen sulfide, were run in the presence of 5.0 PPM of sulfur dioxide. Table 5 is a tabulation of the results. As before, a High-Volume sample air flow rate of 24 CFM was used. Air at a rate of 8.0 lpm of the total was diverted through the canisters. The total recovery of both forms of mercury by the canister averaged 99.6% (σ=9.3%); elemental mercury averaged 98.8% (σ=10.5%); dimethyl mercury recovery was 104.0% (σ=9.2%). Under the conditions of the calibration, it was possible to ascertain that neither the iodine monochloride nor nitric acid-permanganate bubblers performed adequately in the presence of SO_2. While for iodine-monochloride this result conforms with previously published results, the performance of the acid permanganate system is not explained.

On the basis of these data it may be concluded that the two component absorbent canister performs effectively to remove elemental mercury and dimethyl mercury from air in the presence of SO_2. These results are an improvement over the performance of the bubblers under the same conditions.

3.3.5.4 Effects of Nitrogen Dioxide

The canister collection system was further tested under the same operating parameters in the presence of 3.2 PPM of nitrogen

dioxide. The data are compiled in Table 6. Total recovery was 101.0% (σ=5.1%); elemental mercury recovery averaged 101.3% ($\sigma = \pm 4.8\%$); dimethyl mercury recovery was 100.5% (σ=9.6%). In addition, both the iodine monochloride and acid permanganate bubblers performed very well in the presence of NO_2.

3.3.5.5 Summarized Effects of Interferences

No effects of potential interferences are determinable on the basis of the data obtained in collection of elemental and dimethyl mercury by the canister technique in the presence of H_2S, SO_2 and NO_2. Three sets of collection data are shown in Tables 7, 8 and 9. In Table 7, total mercury recovery as determined by canister is recorded against calibration levels in the presence of all three potential interferences. One hundred percent collection efficiency is approached in the presence of H_2S, SO_2 and NO_2. A similar treatment of the data for elemental mercury recovery on 10% silver-alumina has been constructed in Table 8; dimethyl mercury recovery on charcoal is illustrated in Table 9. Conclusions for the latter are the same as for total Hg recovery. These data individually and collectively confirm the results of Sections 3.3.2 and 3.3.3 which were obtained during separate collection of elemental mercury and dimethyl mercury.

Averaging the results for all the 28 tests the following recoveries were achieved. The results are based on the values obtained by the indicated calibration procedures:

	Recovery	Standard Deviation
Total Mercury	99.4%	$\pm$ 6.3%
Elemental Mercury	99.9%	$\pm$7.0%
Dimethyl Mercury	98.2%	$\pm$7.9%

Table 7

Recovery of Elemental and Dimethyl Mercury by

Canister Absorbents in the Presence of H_2S, SO_2 and NO_2

Gas Added	Concentration of Hg and $(CH_3)_2$ Hg in Source ($\mu g/m^3$)	Recovery by Canister Absorbents ($\mu g/m^3$)
H_2S	3.95	3.72
(1.2PPM)	3.95	4.08
"	3.95	3.65
"	3.95	3.87
"	14.25	14.50
"	14.25	14.32
"	14.25	13.30
"	14.25	13.93
"	344.5	349.8
"	344.5	371.7
"	344.5	312.0
"	344.5	325.9
SO_2	5.63	5.61
(5.0PPM)	5.63	5.07
"	5.63	5.02
"	5.63	5.63
"	346.7	388.4
"	346.7	375.7
"	346.7	313.7
"	346.7	309.1
NO_2	8.54	8.11
(3.2PPM)	8.54	8.81
"	8.54	8.32
"	8.54	8.31
"	345.3	366.0
"	345.3	379.8
"	345.3	340.0
"	345.1	346.1

Average Recovery (%) - 99.2

Average Standard Deviation (σ, %) $\pm$ 7.0

Table 8

Recovery of Elemental Mercury by 10% Silver on Alumina

in the Presence of H_2S, SO_2 and NO_2

Gas Added	Concentration of Elemental Hg in Source ($\mu g/m^3$)	Recovery by Silver-alumina ($\mu g/m^3$)
H_2S (1.2PPM)	2.20	2.06
"	2.20	2.42
"	2.20	2.06
"	2.20	2.22
"	10.5	10.8
"	10.5	10.7
"	10.5	9.9
"	10.5	10.4
"	300.0	311.6
"	300.0	325.4
"	300.0	273.8
"	300.0	289.2
SO_2 (5.0PPM)	3.70	3.59
"	3.70	4.14
"	3.70	3.26
"	3.70	3.65
"	300.0	333.0
"	300.0	324.0
"	300.0	270.0
"	300.0	257.4
NO_2 (3.2PPM)	6.60	6.22
"	6.60	6.92
"	6.60	6.45
"	6.60	6.64
"	300.0	318.6
"	300.0	325.6
"	300.0	295.7
"	300.0	298.7

Average Recovery (%) - 99.9

Average Standard Deviation (σ ,%) $\pm$ 6.3

Table 9

Recovery of Dimethyl Mercury
by Charcoal (TCA, Barneby-Cheney)
in Presence of H_2S, SO_2 and NO_2

Gas Added	Concentration of $(CH_3)_2Hg$ in Source ($\mu g/m^3$)	Recovery by Charcoal ($\mu g/m^3$)
H_2S (1.2 PPM)	1.75	1.66
"	1.75	1.66
"	1.75	1.59
"	1.75	1.65
"	3.75	3.70
"	3.75	3.62
"	3.75	3.40
"	3.75	3.53
"	44.5	38.2
"	44.5	46.3
"	44.5	38.2
"	44.5	36.7
SO_2 (5.0PPM)	1.93	2.02
"	1.93	1.93
"	1.93	1.76
"	1.93	1.98
"	46.7	55.4
"	46.7	51.7
"	46.7	43.7
"	46.7	51.7
NO_2 (3.2PPM)	1.94	1.89
"	1.94	1.89
"	1.94	1.87
"	1.94	1.67
"	45.3	47.4
"	45.3	54.2
"	45.3	44.3
"	45.3	47.4

Average Recovery (%) - 98.2

Average Standard Deviation (σ, %) $\pm$ 7.9

In conclusion, the canister collector utilizing 10% silver on alumina and TCA Charcoal does provide a simple method for sampling both ambient atmospheres and severely contaminated environments for all forms of mercury.

3.3.6 Environmental Tests

3.3.6.1 Results

A series of tests of the environment at the GEOMET Pomona Laboratory were carried out as a complete check of the collection and analytical methodology under normal ambient conditions. These tests were conducted over sampling intervals ranging from 7 to 24 hours with the High-Volume sampler operating at 24 CFM. Three positions were selected for tests: (1) a doorway leading to the external atmosphere, (2) a shop area and (3) the laboratory in which the mercury experimentation and analysis was conducted. Table 10 is a compilation of the data.

The initial ambient tests were conducted in the laboratory where the reagents for the program were stored. Air was pulled through the canisters at 9.5 l/min. The air was also sampled by an iodine monochloride bubbler for these runs. Analysis of the canisters showed 0.022-0.028 ($\mu g/m^3$) of elemental mercury and 0.015-0.026 ($\mu g/m^3$) of combined mercury (as Hg). For these tests, the iodine monochloride estimates of total mercury were 0.043-0.049 ($\mu g/m^3$). No particulate mercury was detectable above the values determined as blanks.

Average analysis of the glass fiber filters shows a blank value of 0.67 μg as Hg. A value of 0.05 μg of collected Hg particulates has been selected as the detection threshold. In terms of the air sampled this value has been expressed in various terms, i.e., for a 24 hour sample ($978 m^3$)

Table 10

Ambient Tests at GEOMET Pomona Laboratory

Location	Duration (min)	Canister Analyses: Elem. Hg ($\mu g/m^3$)	Canister Analyses: Comb. Hg ($\mu g/m^3$)	Particle Hg Anal. ($\mu g/m^3$)	High-Vol Air Sampling Rate (CFM)	Canister Air Sampling Rate (l/m)	Air Temperature (^oF)	Humidity (RH)	Independent Hg Anal ($\mu g/m^3$)
External Doorway	1440	0.010	<0.003	$<5\times10^{-5}$	24.0	8.0	48-70	21-68	-
"	1440	0.016	<0.003	$<5\times10^{-5}$	24.0	8.0	42-62	35-62	-
"	1440	0.021	<0.003	3.0×10^{-4}	24.0	8.0	55-75	31-42	22.7** (14.7-28.1)
"	1440	0.015	<0.003	4.6×10^{-4}	24.0	8.0	52-77	35-38	18.9** (15.2-27.2)
"	1440	0.017	<0.003	7×10^{-5}	24.0	8.0	50-74	35-50	15.4** (11.5-16.5)
"	1440	0.024	<0.003	1.7×10^{-4}	24.0	8.0	52-77	36-42	16.9** (12.2-21.0)
"	1440	0.013	<0.003	9.2×10^{-4}	24.0	8.0	55-75	32-53	17.4** (11.8-22.2)
"	1440	0.019	<0.003	1.2×10^{-3}	24.0	8.0	51-75	30-47	18.2** (11.7-25.0)
Shop Area	480	0.044	<0.003	1.5×10^{-4}	24.0	8.0	70-73	52-60	-
Shop Area	480	0.044	<0.003	1.5×10^{-4}	24.0	8.0	71-74	41-51	-
Shop Area	420	0.049	<0.003	1.7×10^{-4}	24.0	8.0	70-76	45-55	-
Shop Area	420	0.025	<0.003	1.7×10^{-4}	24.0	8.0	69-72	33-39	-
Laboratory	480	0.023 0.023	0.016 0.026	1.5×10^{-4}	24.0	9.5	75-77	51-59	0.049*
Laboratory	960	0.022 0.028	0.015 0.021	8×10^{-5}	24.0	9.5	73-75	45-49	0.043*

* by ICl bubbler

** by GEOMET Model 103 Air Monitor, average values. Values in parentheses are extremes of results obtained in 30 minute analyses.

0.05 μg is equivalent to 5×10^{-5} μg/m^3. For shorter determinations the threshold is larger. Values for various sampling intervals are tabulated in Column 5 of Table 10.

Determinations of mercury vapor concentrations in the shop area indicated that the entire mercury content of the air was due to elemental mercury. Values from 0.025 to 0.049 μg/m^3 of elemental mercury were encountered. No determinations by other techniques were made simultaneously.

A number of twenty-four hour tests were carried out in an external doorway leading from the shop area to outdoors. In most of these tests, independent evaluations of the mercury level were made by use of the GEOMET, Model 103, Mercury Air Monitor. Elemental mercury levels ranged from 0.010 to 0.024 μg/m^3 in determinations by the High-Volume method. No organic mercury above the blank was detectable. Particulate mercury ranged from 5×10^{-5} to 1.2×10^{-3} μg/m^3 despite a moderately heavy dust loading on the glass fiber filters. The GEOMET Model 103, set-up to measure elemental mercury exclusively showed mercury levels varying from 0.0154 to 0.0227 μg/m^3 on the average. The Model 103 sampled air at 18 l/min. and produced a print-out every 30 minutes during these operations.

3.3.6.2 Detectability Limits

In establishing the analytical methodology, calibrations of the methods were established against samples of elemental mercury vapor and dimethyl mercury in methanol solutions. The calibration samples were added to the appropriate absorbent (i. e., 10% Ag on alumina in the case of Hg vapor and TCA charcoal in the case of dimethyl mercury) and the

entire extraction and combustion procedures were carried out. The use of a soluble mercury standard added at the reduction step was generally avoided.

On the basis of this full analytical procedure, it was determined that a collection of approximately 30 nanograms of mercury on an absorbent (24 ml volume) represented a reliable detection threshold above the blank values normally observed. That is, an absolute quantition of 30 nanograms of mercury added to the 10% silver-alumina absorbent could be successfully determined with a standard deviation of an average result of $\pm$ 10%. Thus, at a sampling rate of 8.0 l/min. through the canister, levels of elemental mercury equivalent to 2.6 nanograms per meter^3 are detectable in 24 hour collection cycles. This value represents the detection threshold. As in the case of the particulate detection threshold, the value in terms of $\mu g/m^3$, varies with the amount of air collected.

The threshold for organic mercury is somewhat higher than that for elemental vapor. The analytical procedure for charcoal utilizes only one gram of material, representing 8.7% of the total canister charge, whereas the elemental analysis utilizes 10 grams, which is 43% of the total. Thus, the organic threshold is approximately 13 nanograms per meter^3 in a 24 hour collection cycle.

3.3.7 Environmental Effects

During all portions of the experimental testing of the canister method, values of the ambient temperature and relative humidity were compiled. Temperatures ranged from 42 to 81°F at the collection sites; relative humidity varied from 21 to 68%. In the ambient tests described in Section 3.3.6, temperature and humidity variations were relatively

large over a period of 24 hours.

In no case was the efficiency of the collection process demonstrably affected by these environmental variations.

3.3.8 Transportability of Samples

In order for the canister method of collection of mercury samples to have field utility, samples must be mailable to a central laboratory in convenient packaging which is adequate to protect sample integrity for relatively long periods of time. As a test of transportability, canisters containing controlled amounts of mercury were mailed across country and back in standard 13.33 x 4.45 cm mailing tubes. A common place 7.62 x 35.56 cm polyethylene bag* was used as an inner wrapping during the mailing operation.

One blank canister containing no added mercury and one canister which contained 29 nanograms of elemental mercury per gram of silver - alumina absorbent and 29 nanograms of dimethyl mercury (as Hg) per gram of TCA charcoal were sent.

Inspection at the end of the first portion of the trip showed that one end of one mailer had been indented. However, the inner packaging was intact. Some charcoal fines were visible in the inner envelope. Return to the point of origin was accomplished without damage. Thus, the samples had been mailed a distance of approximately 6,000 miles.

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* Available from Bradley's Plastic Bag Company, Downey, California 90241, as Stock No. 314C, size 3 x 14 inches.

Analysis on return of the canisters to the laboratory showed:

	Return	Start
Blank Canister		
Ag/Al_2O_3 Absorbent	< 1.25ng/g	< 1.25ng/g
Charcoal Absorbent	< 1.25ng/g	< 1.25ng/g (as Hg)
Sample Canister		
Ag/Al_2O_3 Absorbent	30.2ng/g	29ng/g
Charcoal Absorbent	31.0ng/g	29ng/g (as Hg)

Thus, within the expected reproducibility of the analyses no noticeable contamination resulted from the shipment of the sample canisters by mail. This simple procedure may be used to ship both collected samples to central sites for analysis and to send blank collection canisters to a field point for use.

3.3.9 Estimates of Collection Capacity

Complete tests of collection capacity of the 10% silver on alumina absorbent for elemental mercury or of the TCA charcoal for $(CH_3)_2$ Hg have not been made.

During the screening tests, elemental mercury at approximately 200 $\mu g/m^3$ was passed through 10 ml beds of the 10% Ag/Al_2O_3 absorbent at flow rates of 4 liters/minute for periods in excess of one day. No breakthrough of mercury vapor was detectable by the GEOMET Mercury Air Monitor. This simple test was considered an adequate test of absorption capacity for the purposes of this method development. However, this test was completely compatible with data previously collected.

In testing absorbents during Contract No. 68-02-0578, elemental mercury at levels of 100 $\mu g/m^3$ was passed through a 6% Ag on alumina preparation at flow rates of 20 CFM for 24 hours. Intermittent sampling showed 99.4% efficiency at the end of that period. In this test, a total of ~ 81.5 mg of mercury was passed through 800g of absorbent without breakthrough. Or, in other units, > 0.1 mg of Hg/g of absorbent was retained.

Interpolating the same figures to the scale utilized in the current program, more than 2.445 mg of mercury would be absorbable in the 24 ml (24g) bed of silver/alumina absorbent. However, under the conditions of current usage: 8 l/min. flow @ 100 $\mu g/m^3$, 1.15 mg of mercury would be passed through the miniaturized bed in 24 hours. This is less than one-half the amount retained by the 6% Ag/Al_2O_3 preparation. Thus, the current 10% Ag/Al_2O_3 preparation should have an operating capability well in excess of 24 hours at exposure levels of 100 $\mu g/m^3$.

The high efficiency-high capacity characteristics are the major advantage of preparations of the type tested: silver on high surface area supports.